ELECTRONIC EFFECTS

OF THE AZO GROUP

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ABSTRACT

The electronic effects of the azo group have been examined in two ways.

Part I. The rates of positive bromination of azoxybenzene and four azobenzenes have been measured in aqueous dioxan. The results are interpreted in terms of partial rate factors and the Hammett equation. Electrophilic para-substituent constants (σ_p^+) are derived for the phenylazo, 3-chlorophenylazo, 3-bromophenylazo, 4-fluorophenylazo, and phenyl-ONN-azoxy substituents. A possible explanation is suggested for the discrepancy in the derived σ_p^+ value of the phenylazo group with literature values.

Part II. The ^{13}C N.M.R. spectra of several substituted ethyl cinnamates, ethyl 4-arylethenylcinnamates, ethyl 4-arylazocinnamates, ethyl 3-arylazocinnamates, and azobenzenes have been measured in deuterochloroform. The attenuation of electronic effects by the 4-ethenylphenylene and the 3- and 4-azophenylene linkages is investigated. The chemical shifts of all carbon atoms in these compounds are discussed in terms of the Dual Substituent Parameter extension of the Hammett equation.

PART I

POSITIVE BROMINATION OF AZOBENZENES AND AZOXYBENZENE

INTRODUCTION

Despite the wide range of uses of azo compounds in organic chemistry, the nature of the azo linkage and its electron donating or accepting properties is poorly understood. The most common azo compounds are those with two aryl groups, i.e. the azobenzenes, and it is these which have received the most attention. In such aromatic systems, the easiest way of investigating electronic effects free from complications of steric origin is by means of the Hammett equation.

Originally, Hammett correlated the rate or equilibrium constants of many reactions with the Ka of benzoic acids:

$$\log \frac{k^X}{k^H} = \rho\sigma$$

where k^X is a rate or equilibrium constant for a meta- or para-X-substituted aromatic, k^H is the corresponding property for the unsubstituted one, ρ is a parameter (the reaction constant) which depends only on the nature of the reaction (including temperature and solvent), and σ is a parameter (the substituent constant) which depends solely on the nature of the substituent. He constructed a scale of substituent constants (σ) by arbitrarily defining $\rho = 1.000$ in the case of benzoic acid ionizations in water at 25^{o}.[1] However, there were a few reactions (notably those of phenols and anilines) which did not correlate well, with σ values for some para-substituents. Accordingly, he set up the σ^- scale for such reactions where direct resonance interaction occurs between a -R substituent and a +R side-chain. Later, Brown and Okamoto[2] set up a similar σ^+ scale for +R

substituents undergoing resonance interaction with a -R side-chain. This scale was based on the solvolysis of aryldimethylcarbinyl chlorides and gives good correlations for electrophilic aromatic substitution. In the case of benzoic acids, a small amount of resonance occurs with +R substituents because of the -R nature of the carboxyl group. Another scale, Taft's σ^{o}, is based on ionization of phenylacetic acids, where no direct resonance interaction can take place.[3] Since there can be no resonance between any meta substituent and a reacting side-chain, it follows that $\sigma_m = \sigma_m^{o} = \sigma_m^{+} = \sigma_m^{-}$. Often it is useful to resolve total electronic effects of a substituent (as expressed by σ) into inductive and resonance components. $\sigma = \sigma_I + \sigma_R$

In the case of the phenylazo substituent, there is general agreement in the literature[4a] in the values for σ_m (+0.28), σ_p (+0.34) and σ_p^{-} (+0.68). The large difference between σ_p and σ_p^{-} indicates that the phenylazo group is a powerful -R substituent. However, this group can also behave as a +R substituent in reactions when called upon to do so, but there is a lack of consistent values of σ_p^{+} reported in the literature.

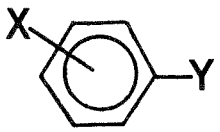
The most studied reactions have been nitration and halogenation, and as a result of these, it was established early on[4b] that the phenylazo group directs incoming electrophiles to the ortho- and para-positions. However, very few kinetic data exist concerning the rates of electrophilic substitution of azobenzenes. Robertson, de la Mare, and Swedlund[5] found that chlorination of azobenzene in aqueous acetic acid at 25^{o} occurred 4.6 times faster (per

phenyl group) than benzene (no product isomer ratios were reported). On the other hand, Robertson, Hitchings and Will[6] reported that a freshly prepared solution of bromine in acetic acid did not react with azobenzene at 35° after 16 hours. They found, however, that the reaction proceeds on addition of hydrogen bromide and they postulated a preliminary addition of HBr across the N=N double bond, so that the species undergoing bromination is not azobenzene. Since then there has been one further kinetic study on electrophilic substitution in azobenzene. Sharnin and Falyakhov[7] calculated a σ_p^+ value of -0.187 based on competitive nitration of azobenzene and naphthalene with nitric acid in acetic anhydride at 0°. One other value of σ_p^+ based on a different reaction is that of Fisher and Meierhoefer[8] who reported a value of -0.15 based on competitive side-chain bromination of p-phenylazotoluene and toluene by N-bromosuccinimide in benzene at 80°; (it has already been shown[9] that this reaction is satisfactorily correlated with σ^+). Another interesting value of σ_p^+ is that determined by Hashida and co-workers.[10] They obtained a value of σ_p = +0.190 based on the diazonium coupling reaction with R-acid. Using a value of σ_p = +0.349 based on p-phenylazobenzoic acid ionization[11] together with a Yukawa-Tsuno factor[12] of r^+ = 0.263, they calculated a value for the phenylazo substituent of σ_p^+ = -0.373.

In view of the lack of agreement between the various results, the value of σ_p^+ for the phenylazo substituent was considered worthy of a closer examination. The reaction system chosen was positive bromination by acidified hypobromous acid. This reaction has been studied by many workers for a

range of compounds in different solvents.[13] The brominating species in the presence of mineral acids is believed to be Br^+ or a solvate. One advantage of this system is that there is no Br^- present and hence no possibility of any preliminary addition of HBr.[6] The bromination of several "activated" aromatics has been carried out by de la Mare and co-workers[14,15,16] in 50% v/v aqueous dioxan using hypobromous acid with dilute perchloric acid. However, all deactivated compounds studied were brominated in water in the presence of more concentrated acid.[17] Accordingly, it was decided to attempt to reproduce the results of de la Mare and Harvey[14] for toluene and benzene, and also to extend the range of the Hammett plot by brominating a deactivated substrate (bromobenzene) in the same solvent. The bromination of azobenzene could then be attempted under similar conditions in order to obtain σ_p^+ for the phenylazo substituent. In addition, it would be of interest to compare σ_p^+ with that obtained for other arylazo substituents and for the related phenyl-ONN-azoxy group, which is also known[4c] to be an ortho/para-director.

Although the electronic effects of other arylazo substituents can be examined in the same way as for the phenylazo group, and σ_p^+ obtained for each one, it is more generally useful to interpret the effects of these substituents using the phenylazo group itself as a reference point. This is done by assuming that the azophenylene bridge is not part of the substituent but part of the side-chain. Then ρ can be found for any of the systems (II), (III), or (IV) and compared to that obtained for system (I).



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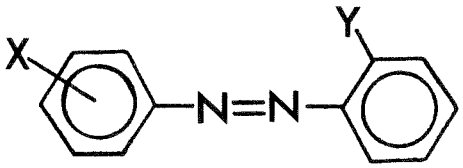

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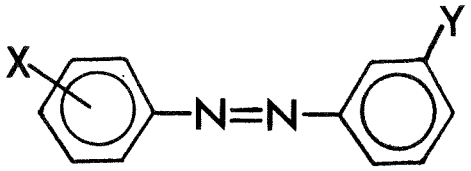

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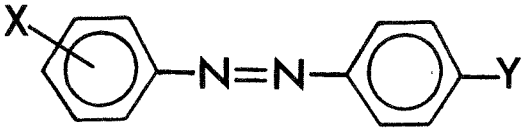


(IV)

This comparison gives a measure of the efficiency of transfer of the effects of the substituent X through that particular azophenylene linkage to the reacting side-chain, Y. The ratio of the two reaction constants is known as the transmission coefficient and is given the symbol π'. The symbols π'_o π'_m and π'_p can be used to refer to system (II), (III), or (IV) respectively.

$$\frac{\rho_{arylazo}}{\rho_{aryl}} = \pi'$$

In the case of electrophilic substitution, because of the predominantly ortho/para-directing nature of arylazo groups and experimental difficulties in analysing mixtures of meta- and para-isomers, transmission through the meta-azophenylene linkage (system III) cannot conveniently be investigated, but the others can. Once ρ has been established for the arylazo series (based only on meta-substituents, since no direct resonance interaction can occur between these substituents and the reacting side-chain), the

extent of direct resonance interaction between +R para-substituents and the reacting side-chain can be estimated by comparing the σ values obtained for these substituents with their established σ and σ^+ values.

It was decided to attempt bromination of the following azobenzenes (in addition to azobenzene itself): 3-chloro, 3-bromo, 3-nitro, 4-fluoro, and 4-dimethylamino.

EXPERIMENTAL

(A) Reagents

Dioxan.

A mixture of technical dioxan (3 ℓ), water (300 ml), and concentrated hydrochloric acid (40 ml) was refluxed for 12 hours, while bubbling a slow stream of nitrogen through it. After cooling, potassium hydroxide flakes (about 1 kg) were added until no more dissolved. The dioxan layer was then decanted off and dried overnight over fresh potassium hydroxide pellets. It was then refluxed over sodium for at least 24 hours, until the sodium remained bright, and finally distilled off sodium and stored in dark bottles filled to capacity and fitted with plastic stoppers.

Perchloric Acid.

Stock solutions of perchloric acid were prepared from A.R. grade 60% perchloric acid, and standardised using A.R. grade borax, with methyl red indicator.

Sodium Thiosulphate Solution.

Sodium thiosulphate pentahydrate (4.9 g, A.R. grade) was dissolved in distilled water (2.2 ℓ), chloroform (10 drops) was added as a preservative, and the mixture was shaken until homogeneous. This was standardised using A.R. grade potassium bromate, with ammonium molybdate as catalyst and starch as indicator.

Starch Solution.

Soluble starch (2.0 g, A.R. grade) was suspended in a few millilitres of distilled water and added to boiling water (200 ml).

Boiling was continued for a further 2 minutes, and after cooling, A.R. grade potassium iodide (4.0 g) was added. The solution was always used fresh.

Hypobromous Acid.[18]

Bromine (2.56 g, 0.0160 mol) was dissolved in distilled water (200 ml), and A.R. grade 88% phosphoric acid (1.0 g, 0.0090 mol) was added. Silver oxide (2.0 g, 0.0086 mol) was added slowly with constant stirring, and the solution was stirred for a further 30-40 minutes, until the supernatant liquid appeared clear when stirring was discontinued. The mixture was then filtered (sintered glass) to remove silver bromide, and distilled under vacuum in the dark at approximately 40^{o}C, using a rotary evaporator. Ice-salt was used to cool both the receiver and the water passing through the condenser. The distillate was extracted three times with sulphur-free carbon tetrachloride in the cold, then centrifuged to remove traces of extractant and diluted two-fold in order to bring it to approximately the right concentration (dilution also improved its keeping qualities). Some of the solution was used immediately. The remainder was stored in the dark under refrigeration. If used within 24 hours, no significant difference in results was observable. The hypobromous acid, when freshly prepared as described above, had a concentration of 0.05 - 0.06 M (before dilution), unlike that prepared by Derbyshire and Waters[18] (0.02 M). Fresh solutions gave no precipitate with silver nitrate, but after a few hours storage a faint turbidity could be observed.

(B) Preparation of Precursors.

Nitrosobenzene

This was prepared by reducing nitrobenzene with zinc powder in aqueous ammonium chloride solution followed by dichromate oxidation, as described in Vogel.[19a] It was steam distilled but not recrystallised, and was stored under refrigeration.

4-Bromonitrosobenzene.[20] 4-Bromonitrobenzene (11.5 g, 0.057 mol) was heated in ethanol (100 ml) until dissolved, and calcium chloride dihydrate (0.5 g) in water (15 ml) was added. This was heated under reflux and 90% zinc powder (10.0 g, 0.138 mol) was added in portions with vigorous stirring. Five minutes after the addition of zinc was complete, the solution was quickly filtered under suction and the zinc residues were washed with hot ethanol. The combined orange filtrate and washings were rewarmed to dissolve any precipitated 4-bromophenylhydroxylamine, and poured with stirring into a previously prepared and filtered solution containing anhydrous ferric chloride (37.0 g, 0.228 mol) and concentrated hydrochloric acid (50 ml) in water (550 ml) cooled with crushed ice (about 200 g). This mixture was left for a few hours with occasional stirring. It was filtered under suction and washed several times with water, until the washings were no longer yellow. The off-white solid was finally steam distilled and air dried under refrigeration. Yield: 2.6 g (25%). It was used without further purification.

(C) Preparation of Substrates.

For column chromatography, Laporte Type H 100-200 mesh alumina was used without deactivation. Benzene and petroleum ether were distilled from phosphorus pentoxide before use. Petroleum ether refers to the fraction boiling between 50-70°. Melting points are uncorrected.

Toluene and Benzene.

A.R. grade toluene and benzene were used without further purification.

Bromobenzene.

Reagent grade bromobenzene was distilled once at atmospheric pressure.

Azobenzene.

Chromatographic standardisation grade azobenzene was used without further purification.

Azoxybenzene.

This was prepared by refluxing nitrobenzene (30 g, 0.24 mol) with sodium hydroxide in methanol, as described in Hickinbottom;[21] the yield of azoxybenzene was 22.8 g (94%). It was recrystallised twice from methanol. After drying over phosphorus pentoxide in the dark, the melting point (very fine pale yellow needles) was 36° (lit. 36°).[21]

4-Fluoroazobenzene.

4-Fluoroaniline (5.1 g, 0.0467 mol) was dissolved in glacial acetic acid (50 ml), steam distilled nitrosobenzene (5.00 g, 0.0467 mol) was added, and the resulting solution was heated on a steam bath for 4 hours. After cooling, the acetic acid was

removed using a rotary evaporator, and the crude product was taken up in ether (100 ml). This was washed quickly with acidified hypobromous acid solution, then water, dilute sodium carbonate solution (twice), and finally with water (twice). It was then dried over anhydrous magnesium sulphate and the ether evaporated off. This crude product was dissolved in the minimum volume of benzene and purified by chromatography on alumina, with petroleum ether as eluent. The orange fraction was recrystallised twice from alcohol and dried over phosphorus pentoxide. Yield: 5.55 g (59%), orange-yellow needles, m.p. 82.5-83^{o} (lit. 83^{o}).[22]

3-Chloroazobenzene and 3-Bromoazobenzene

The same method was used in the preparation of both these compounds. More difficulty was experienced in eliminating all traces of reactive impurities, (presumably anilines), which had the effect of giving an initial rate of reaction which was misleading.

3-Chloroaniline (5.96 g, 0.0467 mol), or 3-bromoaniline (8.03 g, 0.0467 mol), was dissolved in glacial acetic acid (50 ml), steam distilled nitrosobenzene (5.00 g, 0.0467 mol) was added, and the resulting solution was heated on a steam bath for 4 hours. After cooling, the acetic acid was taken off using a rotary evaporator. The residue was dissolved in benzene (60 ml), washed with dilute sodium carbonate solution (twice) and with water (twice). The benzene solution was dried over anhydrous magnesium sulphate, and concentrated. It was then passed through an alumina column eluting with petroleum ether, with benzene added as required. After removal of the solvent,

the product was dissolved in ether (100 ml) and washed twice with hypobromous acid solution to which some perchloric acid had been added, twice with 5% sodium thiosulphate solution, twice with sodium carbonate solution, and finally three times with water. After drying with anhydrous magnesium sulphate and evaporating the ether, the compound was recolumned on alumina as before. The solvent was evaporated off and the compound recrystallised from absolute alcohol, then dried over phosphorus pentoxide.

Yields: 3-Cl: 6.65 g (66%), orange needles, m.p. 68° (lit. 68°).[23]

3-Br: 8.39 g (69%), orange needles, m.p. 69° (lit. 69°).[24]

3-Nitroazobenzene.

3-Nitroaniline (6.50 g, 0.0471 mol) was dissolved in glacial acetic acid (35 ml), nitrosobenzene (5.00 g, 0.0467 mol) was added, and the resulting solution was heated on a steam bath for 4 hours. After cooling, the acetic acid was taken off using a rotary evaporator. Benzene (60 ml) was added, and the crude product was washed twice with dilute sodium carbonate solution and twice with water. Drying over anhydrous magnesium sulphate and concentrating the solution, were followed by column chromatography through alumina, using mixtures of benzene and petroleum ether to elute. After evaporating the solvent, the compound was recrystallised from absolute alcohol and dried over phosphorus pentoxide. Yield: 3.49 g or 33%, orange needles, m.p. 97-97.5° (lit. 96°).[25]

4-N,N-Dimethylaminoazobenzene.

Indicator grade Methyl Yellow was dissolved in hot ethanol, filtered, and recrystallised from ethanol/water.

(D) Preparation of Products for Identification Purposes

Dibromobenzenes.

These were available commercially.

4-Bromoazobenzene, 4-Bromoazoxybenzene, and mixture of 4- and 4'-Bromoazoxybenzene.

These were available in the department, having been used for previous studies.

4-Bromo-4'-fluoroazobenzene.

4-Fluoroaniline (0.59 g, 0.0053 mol) was dissolved in glacial acid (30 ml), steam distilled 4-bromonitrosobenzene (1.0 g, 0.0054 mol) was added, and the solution heated on a steam bath for 4 hours. After cooling, the acetic acid was removed under reduced pressure and the crude product was dissolved in benzene (50 ml), washed twice with dilute sodium carbonate solution, twice with water, and dried over anhydrous magnesium sulphate. After reducing the volume to 2-3 ml, the product was purified by chromatography on alumina, eluting with petroleum ether. Recrystallisation twice from ethanol gave fine pale orange crystals with melting point 98-104^{o} (lit. 135^{o}).[26] It was found to contain a significant amount of p-bromonitrosobenzene (identified by G.L.C. retention time and by smell), but for the purpose for which it was to be used further purification was considered unnecessary. Yield: 0.13 g (9%, impure).

4-Bromo-3'-chloroazobenzene.

Using the above method, 0.67 g (0.0053 mol) of 3-chloroaniline gave 0.56 g (36%) of orange needles, m.p. 119^{o} (lit. 119^{o}).[27]

3,4'-Dibromoazobenzene.

Again using the above method, 0.91 g (0.053 mol) of 3-bromoaniline gave 0.34 g (19%) of orange needles, m.p. 129° (lit. 126°).[27]

(E) Method.

(1) Kinetics of Disappearance of Hypobromous Acid.[14]

The reactions were carried out in black-painted stoppered flasks immersed in a water bath at 25°. Because of the limited solubility of some substrates in 50% aqueous dioxan, these (after being weighed out) were first dissolved in dioxan, then the required amount of water and perchloric acid was added slowly, with stirring. In the case of volatile substrates, these were weighed out directly into the dioxan. The reaction was started by addition of the hypobromous acid, using a pipette. A blank determination was carried out on each occasion using solutions prepared in exactly the same way, including the use of dioxan from the same bottle as that used for the run. The reactions were followed iodometrically, by quenching a known volume of mixture with an excess of 1% aqueous potassium iodide solution, and titrating with standard sodium thiosulphate solution. Freshly prepared starch solution was used as indicator, and each aliquot was diluted with an approximately equal volume of distilled water before the endpoint. This made the endpoint easier to observe.

Pseudo-first-order rate constants were obtained by plotting graphs of ln (titre) against time for both blank and run and finding the slopes. The method of initial rates used by de la Mare and Harvey[14] was found to give results which were

in good agreement with those obtained by this method, but suffered from the fact that extrapolation of k_1 to t=0 was unreliable in the case of less reactive compounds because the random scatter in the titres was more significant for these compounds. Typical conditions used for each substrate are summarised in Table I.

Table I

Typical conditions used for each substrate

Substrate	[ArH]	[$HClO_4$]	[HOBr]
Toluene	0.008-0.009M	0.003M	0.0006-0.0014M
Benzene	0.014-0.017M	0.06-0.08M	0.0011-0.0014M
Bromobenzene	0.044-0.052M	0.16-0.20M[a]	0.0013-0.0015M
Azobenzene	0.014-0.016M	0.08-0.20M[b]	0.0012-0.0015M
Azoxybenzene	0.010-0.015M	0.006-0.20M	0.0012-0.0014M
4-Fluoroazobenzene	0.0095-0.0097M	0.16-0.20M	0.0013-0.0016M
3-Chloroazobenzene	0.0069-0.0075M	0.20M	0.0011-0.0014M
3-Bromoazobenzene	0.0055-0.0060M	0.20M	0.0010-0.0013M
3-Nitroazobenzene	0.0067M	0.20M	0.00135M
4-N,N-dimethylaminoazobenzene[c]	0.004M	0.0015M	0.004-0.008M

a. 0.40M was also used, but it was found that at this acid concentration k_3 had increased nearly two-fold. For this reason, the maximum [$HClO_4$] used in any run was 0.20M.

b. Lower concentrations were also used, but this made the value obtained for k_3 less reliable.

c. Only preparative runs were carried out with this compound (see text).

In the case of dimethylaminoazobenzene a preparative run was first undertaken to ascertain whether 4-bromo-4'-N,N-dimethylaminoazobenzene would be formed under the reaction conditions. Equimolar quantities of hypobromous acid and

dimethylaminoazobenzene were allowed to react in 50% aqueous dioxan for 24 hrs at 25°. The dioxan was then removed using a rotary evaporator, the resulting suspension neutralised by the addition of solid sodium carbonate (until effervescence ceased) and the mixture extracted twice with benzene. After drying the benzene extracts over anhydrous magnesium sulphate, the solvent was removed and a ^{13}C N.M.R. spectrum of the product was obtained in deuterochloroform solution.

A similar run with a two-fold excess of hypobromous acid led to an immediate yellow turbidity. The hypobromous acid was all immediately consumed (as indicated by starch-iodide paper). The mixture was left for 1½ hours. After this time, it was still opaque with a small amount of orange oil floating on the surface. This was worked up as described above. Two runs were also carried out with molecular bromine as the brominating agent; one with equimolar bromine, the other with a two-fold excess. The solutions were left for about 30 minutes and worked up as before, except that no sodium carbonate was added.

The ^{13}C N.M.R. results all showed the presence of products of bromination ortho to the dimethylamino group, but no sign of any 4-bromo-4'-N,N-dimethylaminoazobenzene. For this reason, no kinetic measurements were attempted.

(2) Determination of Isomer Ratios.

The isomer ratios for toluene have already been reported by de la Mare and Harvey,[14] and in the case of benzene, only one isomer is formed. For all other compounds, the ratios were determined by gas liquid chromatography, using a "Varian 1440" gas chromatograph on F.I.D. mode and a "Kent Chromalog"

integrator. In a few cases, the accuracy of the machine integrator was checked by the method of cutting and weighing the peaks, and also by counting the squares under the peaks.

In most cases, only two well-separated product peaks were obtained. The para-isomer was identified by addition of an authentic sample, which was found to increase the size of one peak, without the appearance of any "shoulders". In the case of azoxybenzene, a mixture of 4- and 4'-bromo-azoxybenzene was also added to a sample of the product mixture. An extra peak appeared between the two main ones. Therefore it can be concluded that no 4'-bromoazoxybenzene is formed during the reaction. (It is also interesting to note that azoxybenzene was the only substrate for which the para-product had a longer retention time than the ortho-product.)

Previous studies[28] had shown that meta- and para-isomers could not be resolved by G.L.C., so the "para" peaks were in fact "meta + para" peaks. In calculating final k_3^{para} values, the contribution due to the meta-isomer was estimated indirectly and allowance was made for its presence (see Discussion).

As a further aid to product identification, G.C.-M.S. studies were carried out on the reaction products of azoxybenzene, 4-fluoroazobenzene, 3-bromoazobenzene, and 3-chloroazobenzene, using a Hewlett Packard 5982A G.C.-M.S. system. In all cases, the two major peaks (aside from starting material) were found to be monobromination products. In the case of 4-fluoroazobenzene, both products were conclusively found from their fragmentation patterns to contain the F and

Br in different rings. In the case of 3-chloro- and 3-bromoazobenzene, traces of ions were found whose source could only be a parent ion with Br and X (X = Cl, Br) in the same ring. However, the major ions were those arising from parent ions with Br and X in different rings. Calculations were carried out to estimate the rate of bromination in the substituted ring, and due allowance was made for the presence of the resulting products. Another useful result obtained from G.C.-M.S. was that a small but significant peak which occurred just before the two main ones in the case of 3-chloroazobenzene, was not a bromination product and could be ignored for the purposes of integration.

Procedure for Work-up of Samples.

The remaining solutions from two or three runs were combined after at least 48 hours had lapsed, and most of the dioxan was removed, using a rotary evaporator. The remaining aqueous suspension was then extracted twice with a small amount of benzene. The benzene extract was dried over anhydrous magnesium sulphate, and concentrated down to a small volume.

Typical G.L.C. conditions for each mixture are summarised in Table II.

Table II

Typical G.L.C. conditions used to separate product isomers.

Substrate	Column.[a]	Temperature.	N_2 flow rate.[b]
Bromobenzene	A	90°	3.5
Azobenzene	A	170°	2.0
Azoxybenzene	A	180°	3.5
4-Fluoroazobenzene	B	160°	3.0
3-Chloroazobenzene	B	170°	3.0
3-Bromoazobenzene	B	180°	3.0

a. Columns used : A. 3% FFAP on Varaport 30; 2.0 metres.

B. 3% OV275 on Chromosorb W; 2.5 metres.

b. Arbitrary units on chromatograph used.

RESULTS

The results obtained from a typical run for azobenzene are given below:

Concentration of azobenzene = 0.01553 M

Concentration of perchloric acid = 0.1590 M

Concentration of hypobromous acid = 0.00124 M

Aliquots of 25 ml were taken at intervals and titrated with 0.00922 M sodium thiosulphate solution.

Run

Time (min).	Titre (ml).	ln (titre).
1.62	6.45	1.864
4.73	6.04	1.798
7.57	5.67	1.735
10.38	5.37	1.681
16.25	4.76	1.560
21.75	4.13	1.418

Blank

Time (min).	Titre (ml).	ln (titre).
3.28	6.67	1.898
6.06	6.63	1.892
8.97	6.56	1.881
12.19	6.49	1.870
17.78	6.42	1.859
23.20	6.31	1.842

Plots of ln (titre) against time for blank and run gave straight lines with no noticeable curvature. A least squares linear regression gave the following parameters:

Run: Regression Parameters: r = 0.9989

SD/RMS = 0.0045

ln (titre) at t=0: a = 1.903, which gives a titre at t=0 of 6.71 ml.

Slope: $b = 0.0218\ min^{-1}$

Blank: Regression Parameters: r = 0.9964

SD/RMS = 0.0010

ln (titre) at t=0: a = 1.907, which gives a titre at t=0 of 6.73 ml.

Slope: $b = 0.0028\ min^{-1}$

The difference of the slopes gives the corrected first order rate constant:

$$k_1 = 0.0190\ min^{-1}$$

Therefore $k_2 = 1.22\ \ell\ mol^{-1}\ min^{-1}$

$$k_3 = 7.69\ \ell^2\ mol^{-2}\ min^{-1}$$

$$= 0.128\ \ell^2\ mol^{-2}\ sec^{-1}$$

The concentrations used and rate constants obtained in individual runs are listed in the following pages, together with the average value and estimated reliability of the third order rate constant for each compound. No reliable result could be obtained for 3-nitroazobenzene, because the slopes of the run and blank were the same, within the usual observed experimental scatter.

Also listed are the product isomer ratios obtained by G.L.C. The figures quoted are the averages of many determinations, together with their standard deviations.

In all runs the solvent was 50% v/v aqueous dioxan and the temperature was 25.0^{o}.

Toluene

Run No.	1	2	3
[Aromatic] (M)	0.00897	0.00836	0.00850
[$HClO_4$] (M)	0.00304	0.00304	0.00304
[HOBr] (M)	0.00065	0.00130	0.00142
Run k_1 (min^{-1})	0.0408	0.0354	0.0376
Blank k_1 (min^{-1})	0.0040	0.0028	0.0023
Corrected k_1 (min^{-1})	0.0368	0.0326	0.0353
k_3 (ℓ^2 mol^{-2} min^{-1})	1350	1280	1370

Average k_3 = 1330 ℓ^2 mol^{-2} min^{-1}

k_3 = 22.2 ℓ^2 mol^{-2} sec^{-1}

Estimated reliability = ± 5%

Benzene

Run No.	1	2	3	4	5
[Aromatic] (M)	0.0144	0.0145	0.0145	0.0145	0.0167
[$HClO_4$] (M)	0.0631	0.0631	0.0631	0.0659	0.0816
[HOBr] (M)	0.00119	0.00116	0.00123	0.00140	0.00134
Run k_1 (min^{-1})	0.0339	0.0364	0.0308	0.0341	0.0452
Blank k_1 (min^{-1})	0.0055	0.0056	0.0029	0.0043	0.0016
Corrected k_1 (min^{-1})	0.0284	0.0308	0.0279	0.0298	0.0436
k_3 (ℓ^2 mol^{-2} min^{-1})	31.3	33.7	30.5	31.2	32.0

Average k_3 = 31.7 ℓ^2 mol^{-2} min^{-1}

k_3 = 0.528 ℓ^2 mol^{-2} sec^{-1}

Estimated reliability = ± 5%

Bromobenzene

Run No.	1	2	3	4	5
[Aromatic] (M)	0.0525	0.0519	0.0507	0.0521	0.0440
[$HClO_4$] (M)	0.159	0.159	0.200	0.199	0.199
[HOBr] (M)	0.00137	0.00141	0.00149	0.00141	0.00140
Run k_1 (min^{-1})	0.0140	0.0142	0.0168	0.0169	0.0149
Blank k_1 (min^{-1})	0.0030	0.0028	0.0029	0.0037	0.0036
Corrected k_1 (min^{-1})	0.0110	0.0114	0.0139	0.0132	0.0113
k_3 (ℓ^2 mol^{-2} min^{-1})	1.32	1.38	1.37	1.27	1.29

Average k_3 = 1.33 ℓ^2 mol^{-2} min^{-1}

k_3 = 0.0222 ℓ^2 mol^{-2} sec^{-1}

Estimated reliability = ± 5%.

Product isomer ratio: %(m + p) = 51.6(±0.4)%

Azobenzene

Run No.	1	2	3	4	5
[Aromatic] (M)	0.0143	0.01536	0.01553	0.01533	0.01613
[$HClO_4$] (M)	0.0795	0.1590	0.1590	0.1992	0.1992
[HOBr] (M)	0.00130	0.00133	0.00124	0.00150	0.00151
Run k_1 (min^{-1})	0.0150	0.0221	0.0218	0.0260	0.0261
Blank k_1 (min^{-1})	0.0064	0.0037	0.0028	0.0025	0.0016
Corrected k_1 (min^{-1})	0.0086	0.0184	0.0190	0.0235	0.0245
k_3 (ℓ^2 mol^{-2} min^{-1})	7.6*	7.53	7.69	7.70	7.63

*Not used for average

Average k_3 = 7.64 ℓ^2 mol^{-2} min^{-1}

k_3 = 0.127 ℓ^2 mol^{-2} sec^{-1}

Estimated reliability = ± 5%

Product isomer ratio: %(m+p) = 47.2(±0.2)%

Azoxybenzene

Run No.	1	2	3	4	5
[Aromatic] (M)	0.01238	0.0107	0.0100	0.0154	0.0125
[$HClO_4$] (M)	0.00607	0.159	0.163	0.199	0.199
[HOBr] (M)	0.00140	0.00135	0.00141	0.00120	0.00141
Run k_1 (min^{-1})	0.0037	0.0368	0.0322	0.0642	0.0484
Blank k_1 (min^{-1})	0.0023	0.0056	0.0030	0.0080	0.0036
Corrected k_1 (min^{-1})	0.0014	0.0312	0.0292	0.0562	0.0448
k_3 (ℓ^2 mol^{-2} min^{-1})	19*	18.3	17.9	18.3	18.0

*Not used for average

Average k_3 = 18.1 ℓ^2 mol^{-2} min^{-1}

k_3 = 0.302 ℓ^2 mol^{-2} sec^{-1}

Estimated reliability = ± 5%

Product isomer ratio: %(m+p) = 52.4(±0.3)%

4-Fluoroazobenzene

Run No.	1	2	3	4	5
[Aromatic] (M)	0.00954	0.00950	0.00954	0.00965	0.00957
[$HClO_4$] (M)	0.163	0.203	0.203	0.203	0.203
[HOBr] (M)	0.00135	0.00156	0.00158	0.00138	0.00139
Run k_1 (min^{-1})	0.0086	0.0105	0.0104	0.0106	0.0104
Blank k_1 (min^{-1})	0.0029	0.0044	0.0033	0.0038	0.0026
Corrected k_1 (min^{-1})	0.0057	0.0061	0.0071	0.0068	0.0078
k_3 (ℓ^2 mol^{-2} min^{-1})	3.7	3.2	3.7	3.5	4.0

Average k_3 = 3.6 ℓ^2 mol^{-2} min^{-1}

k_3 = 0.060 ℓ^2 mol^{-2} sec^{-1}

Estimated reliability = ± 10%

Product isomer ratio: %(m+p) = 46.0(±0.5)%

3-Chloroazobenzene

Run No.	1	2	3	4	5
[Aromatic] (M)	0.00755	0.00706	0.00721	0.00691	0.00695
[$HClO_4$] (M)	0.203	0.203	0.203	0.203	0.203
[HOBr] (M)	0.00132	0.00133	0.00136	0.00136	0.00116
Run k_1 (min^{-1})	0.0062	0.0060	0.0056	0.0064	0.0043
Blank k_1 (min^{-1})	0.0035	0.0033	0.0028	0.0043	0.0017
Corrected k_1 (min^{-1})	0.0027	0.0027	0.0028	0.0021	0.0026
k_3 ($\ell^2\ mol^{-2}\ min^{-1}$)	1.8	1.9	1.9	1.5	1.8

Average k_3 = 1.8 $\ell^2\ mol^{-2}\ min^{-1}$

k_3 = 0.030 $\ell^2\ mol^{-2}\ sec^{-1}$

Estimated reliability = ± 20%

Product isomer ratio: %(m+p) = 56.3(±0.5)%

3-Bromoazobenzene

Run No.	1	2	3
[Aromatic] (M)	0.00599	0.00579	0.00572
[$HClO_4$] (M)	0.203	0.203	0.203
[HOBr] (M)	0.00129	0.00110	0.00124
Run k_1 (min^{-1})	0.0080	0.0046	0.0043
Blank k_1 (min^{-1})	0.0064	0.0033	0.0026
Corrected k_1 (min^{-1})	0.0016	0.0013	0.0017
k_3 ($\ell^2\ mol^{-2}\ min^{-1}$)	1.3	1.1	1.5

Average k_3 = 1.3 $\ell^2\ mol^{-2}\ min^{-1}$

k_3 = 0.022 $\ell^2\ mol^{-2}\ sec^{-1}$

Estimated reliability = ± 20%

Product isomer ratio: %(m+p) = 56.2(±0.7)%

DISCUSSION

Summary of Results

A summary of third order rate constants obtained, together with product isomer ratios is given in Table III. The value of k_3 for toluene agrees well with that of de la Mare and Harvey,[14] but the figure for benzene (0.528) is lower than theirs (0.598) by about 10%.

Table III

Summary of rate constants and isomer ratios.

Compound	Rate constant[a]	Isomer ratio
Toluene	2.22×10^{1}	27.4% (p)[b] 2.3% (m)[b]
Benzene	5.28×10^{-1}	-
Bromobenzene	2.22×10^{-2}	51.6% (m+p)
Azobenzene	1.27×10^{-1}	47.2% (m+p)
Azoxybenzene	3.02×10^{-1}	52.4% (m+p)
4-Fluoroazobenzene	6.0×10^{-2}	46.0% (m+p)
3-Chloroazobenzene	3.0×10^{-2}	56.3% (m+p)
3-Bromoazobenzene	2.2×10^{-2}	56.2% (m+p)

a. Third order rate constant, k_3 expressed in $\ell^2\ mol^{-2}\ sec^{-1}$

b. Determined by de la Mare and Harvey.[14]

Partial Rate Factors

The most convenient way of interpreting the third order rate constants in terms of substitution rates at the various positions, is by means of partial rate factors (f). These are defined as the rate of attack at a particular position relative to the rate of the same reaction at one position of benzene. If the substrates are all considered as monosubstituted benzenes, the partial rate factors are expressed as follows:

$$f_o^X = k_3^X \times \frac{\%ortho}{100} \times \tfrac{1}{2} / \frac{k_3^H}{6}$$

$$f_m^X = k_3^X \times \frac{\%meta}{100} \times \tfrac{1}{2} / \frac{k_3^H}{6}$$

$$f_p^X = k_3^X \times \frac{\%para}{100} / \frac{k_3^H}{6}$$

The partial rate factors for toluene have been determined previously.[14] For the other compounds, f_o can be computed from the percentage of ortho-product formed, but the calculation of f_p is not so simple. This is because the analytical method used (G.L.C.) did not permit the separation of the meta- and para-isomers. For most substituents which are known to be ortho/para- directing in electrophilic substitution, this is not a serious problem because the amount of meta-product is relatively small and can be ignored. The reason for this is (using the terminology of the Hammett equation) that usually σ_p^+ is much more negative than σ_m, and ρ is high (mostly in the range -4 to -10). Using the reported value of ρ for positive bromination in 50% aqueous dioxan (-5.9)[29] together with literature values of σ_m for the bromo[30] and phenylazo[4a]

substituents (+0.39 and +0.28 respectively) an estimate can be made of k_3^{meta} for these compounds, and k_3^{para} obtained by subtraction. These k_3^{para} values are converted to partial rate factors in the usual way.

No σ_m values have been reported for any of the other substituents studied. In the case of the phenyl-ONN-azoxy group, a rough estimate can be made by comparing σ_m for the pyridine aza nitrogen with that of its N-oxide.[31] The introduction of the oxygen makes the latter group more electron withdrawing. On this basis, σ_m for the phenylazoxy group should be greater than that for phenylazo, but it is difficult to say by how much. If a lower limit of +0.30 is assigned to it, the amount of meta-product is less than 2% of the total meta- and para-product.

A greater problem arises in trying to estimate k_3^{meta} (and hence k_3^{para}) for the three halogenoazobenzenes studied, because this requires a knowledge of how efficiently the electronic effects of a substituent in one ring are transmitted to the meta- and para-positions of the other. It can reasonably be expected that transmission to the para-position would be more efficient. In that case, this position would be deactivated more strongly by electron-withdrawing substituents and the relative amount of meta-product would increase. To overcome this difficulty, it was decided to consider the effects of two extreme assumptions together with one that was thought to be more reasonable than either. These assumptions were:

(a) A substituent in one ring has a negligible effect on the electron density at the meta-position of the other; i.e. $\pi'_m = 0$.

(b) A substituent in one ring has the same effect on both the meta- and para-positions of the other; i.e. $\pi'_m = \pi'_p$.

(c) Transmission to the meta-position of the other ring is half as efficient as that to the para-position; i.e. $\pi'_m = \frac{1}{2}\pi'_p$. Alternative (c) is based on the results obtained from the ^{13}C N.M.R. study contained in Part II of this thesis.

Further uncertainty exists in the case of 4-fluoroazobenzene, concerning the appropriate σ value for attack at the 3'-position. Again on the basis of the ^{13}C N.M.R. study (Part II), the same value as for 4'-attack was used. This is reasonable, considering the degree of resonance that would be expected to exist between the +R fluoro group and the -R azo group, which are para-orientated to each other. In practice, it was found that even a value of +0.34 (based on the assumption that $\sigma_m = \sigma_p$ in this case) had a negligible effect on σ_p^+ for the 4-fluorophenylazo substituent (about 0.01 σ unit).

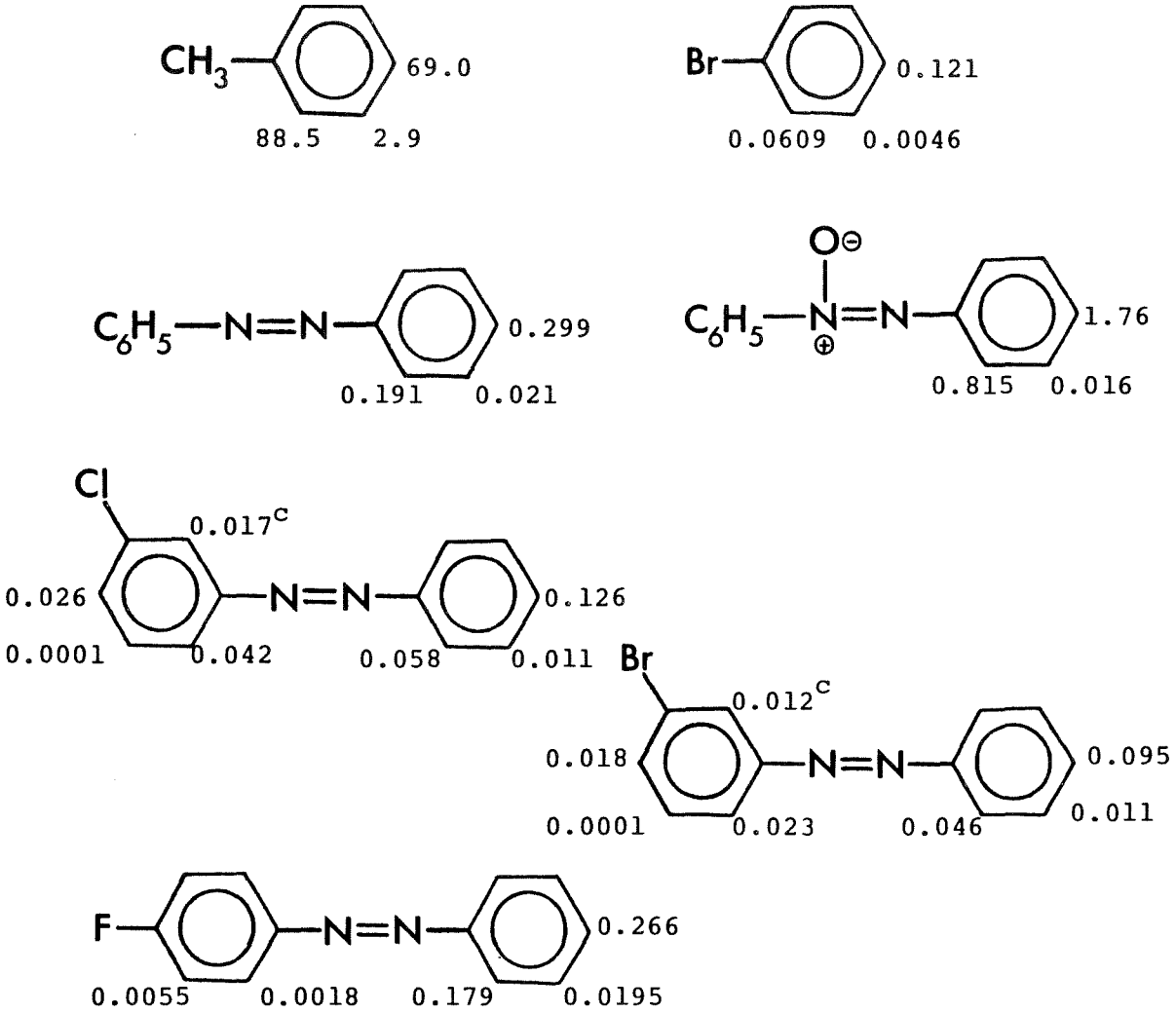
Finally, consideration must be given to possible contributions to k_3 from attack on the other aromatic nucleus. In the case of azoxybenzene, it is expected that this would be insignificant and this is substantiated by G.L.C. The 3'-product which would be formed should have a similar retention time to the 4'-product, and none of the latter was detected. For the halogenoazobenzenes, partial rate factors were estimated by assuming a simple additivity of substituent

constants, together with the ρ value obtained in this study. The measured rate constants were then corrected for this. A summary of all partial rate factors measured or estimated, is given in Fig. I.

The correction for meta-product formation is not significant for azoxybenzene, but is certainly more important for bromobenzene and azobenzene, where the amount of meta-product amounts to 7% and 12% respectively of the total meta- and para-product. The case of 4-fluoroazobenzene is interesting because according to the calculations carried out, the potential amount of meta-product is roughly the same as that in azobenzene, and was not much affected by the various assumed values of π'_m. They also showed that over 97% of the product should arise from bromination of the unsubstituted ring. Unfortunately, this did not prove to be true for 3-chloro- and 3-bromoazobenzene. For these, a substantial amount (roughly 20%) of product was expected with both halogen atoms in the same ring, but their presence could not be established with certainty. It was felt that a comprehensive analysis of these systems involving the synthesis of a considerable number of dibromo- and bromochloroazobenzenes, would not yield enough additional information to make the exercise worthwhile. The listed values of both f_o and f_p for these compounds are based on the assumption that the only products present in the G.L.C. analysis were those of attack at the ortho-, meta-, and para-positions of the unsubstituted ring, and should accordingly be treated with extreme caution, even though

Fig. I

Partial rate factors for positive bromination at 25°C.[a,b]



a. For azoxybenzene, partial rate factors in the other ring (C_6H_5-) were negligible; i.e. all less than f_m.

b. Partial rate factors for the halogenoazobenzenes are based on assumption (c), viz. $\pi'_m = 0.12$ (see text).

c. The partial rate factor in the 2-position of the 3-halogenoazobenzenes is a maximum, with no allowance being made for two ortho-interactions. The actual figure would be lower than this.

the assumption is supported by the G.C.-M.S. studies carried out. Because of the similarity of σ_m values for the chloro and bromo substituents (+0.37 and +0.39 respectively[30]), the rates of bromination in the opposite ring should be very similar in both cases. The differences in f_o and f_p values given are slightly higher than expected but they are in the right order.

The Ortho/Para Ratios.

The ortho/para ratios determined, are listed in Table IV.

Table IV

Ortho/para ratios for positive bromination at 25°C.

Compound	ortho:para
Toluene[a]	2.57:1
Bromobenzene	1.01:1
Azobenzene	1.28:1
Azoxybenzene	0.92:1
3-Chloroazobenzene	0.92:1
3-Bromoazobenzene	0.96:1
4-Fluoroazobenzene	1.34:1

a. From the data of de la Mare and Harvey.[14]

Except for toluene, none of the others have been determined previously. The ratio for bromobenzene is about 1:1 implying that each ortho-position is half as reactive as the para-position. The situation for toluene on the other hand, is reversed, with each ortho-position being about 1.3 times more reactive than the para-position. Assuming comparable steric effects, this is best explained in terms of an inductive

effect which manifests itself more strongly in the ortho-positions. Differences in inductive effects can also be invoked to explain the difference in the ortho/para ratios of bromobenzene and azobenzene, provided that steric effects are roughly constant - the σ_I values for the phenylazo and bromo substituents are +0.25 and +0.44 respectively.[32a] Using this approach, it would be expected that the introduction of a -I group in the azobenzene molecule will decrease the ortho/para ratio in the other ring. This is indeed the case for the 3-chloro and 3-bromo compounds, but not for 4-fluoroazobenzene, which has an ortho/para ratio very similar to azobenzene itself. It is possible that the +R effect of the F influences the electronegativity of the N more distant from it by resonance interaction, and thus changes the inductive effect of the substituent as a whole (resonance-induced inductive effect). This apparent confusion between inductive and resonance effects also shows up in the ^{13}C N.M.R. studies (see p. 102).

The significantly lower ortho/para ratio of azoxybenzene compared to that for azobenzene can also be explained by the expected higher σ_I of the phenyl-ONN-azoxy substituent (see earlier), but it is also possible that this is the result of a change in steric effects.

Of further interest is the comparison of the ortho/para ratios of positive bromination with those of other electrophilic substitution reactions. Of the compounds studied in the present work, relevant data exist only for toluene and bromobenzene. In both compounds the relative amount of ortho-product is usually higher for positive bromination, which suggests that

the attacking electrophile is small, or, more accurately, that there is less steric hindrance to attack by this electrophile. Table V lists the ortho/para ratios for a few typical substitution reactions on toluene and bromobenzene.

Table V

Ratios of isomers formed (ortho/para) in typical electrophilic substitution reactions.

Toluene

Reaction (all at 25°)	ortho:para	Reference
Cl_2, HOAc	1.51:1	33
HNO_3, $MeNO_2$	1.70:1	34
HNO_3, Ac_2O	1.87:1	34
NO_2BF_4, $C_4H_8SO_2$	2.06:1	35a
$HOBr/HClO_4$, 50% $C_4H_8O_2/H_2O$	2.57:1	14

Bromobenzene

Reaction (all at 25°)	ortho:para	Reference
Cl_2, 60% $HOAc/H_2O$	0.63:1	29
HNO_3, $MeNO_2$	0.58:1	36
HNO_3 Ac_2O	0.72:1	37
NO_2BF_4, $C_4H_8SO_2$	0.35:1	35b
$HOBr/HClO_4$, 50% $C_4H_8O_2/H_2O$	1.01:1	This work

Hammett Correlations

In dealing with the magnitude and nature of the various electronic factors involved in the substitution process, Hammett correlations are more useful than partial rate factors. Previous studies of positive bromination under the conditions used here, have yielded ρ values of -5.8[2] and -5.9.[29] However, these figures were obtained using only compounds more reactive than benzene. When data for benzoic acid and nitrobenzene are included, the value of ρ is found to be -6.2.[17] These deactivated compounds were brominated in a much higher acid concentration than that used here, and a different solvent (water only) was used. During the present investigation, it was found that significant deviations in k_3 commenced at a much lower acid concentration than that used by those workers. Using the σ^+ values of Brown and Okamoto,[2] a recalculation of ρ based on the data obtained here for toluene, benzene, and bromobenzene, gave a figure of -5.99, in good agreement with earlier values. The Hammett plot is shown in Fig. II. This was used to determine σ_p^+ for those substituents not used to define ρ, and these are shown in Table VI. Of these substituents, σ_p^+ has been reported previously only for the phenylazo substituent. These values are summarised in Table VII, and it will be noted that they are all much more negative than that reported here.

Hammett plot for positive bromination in 50% dioxan at 25°C.

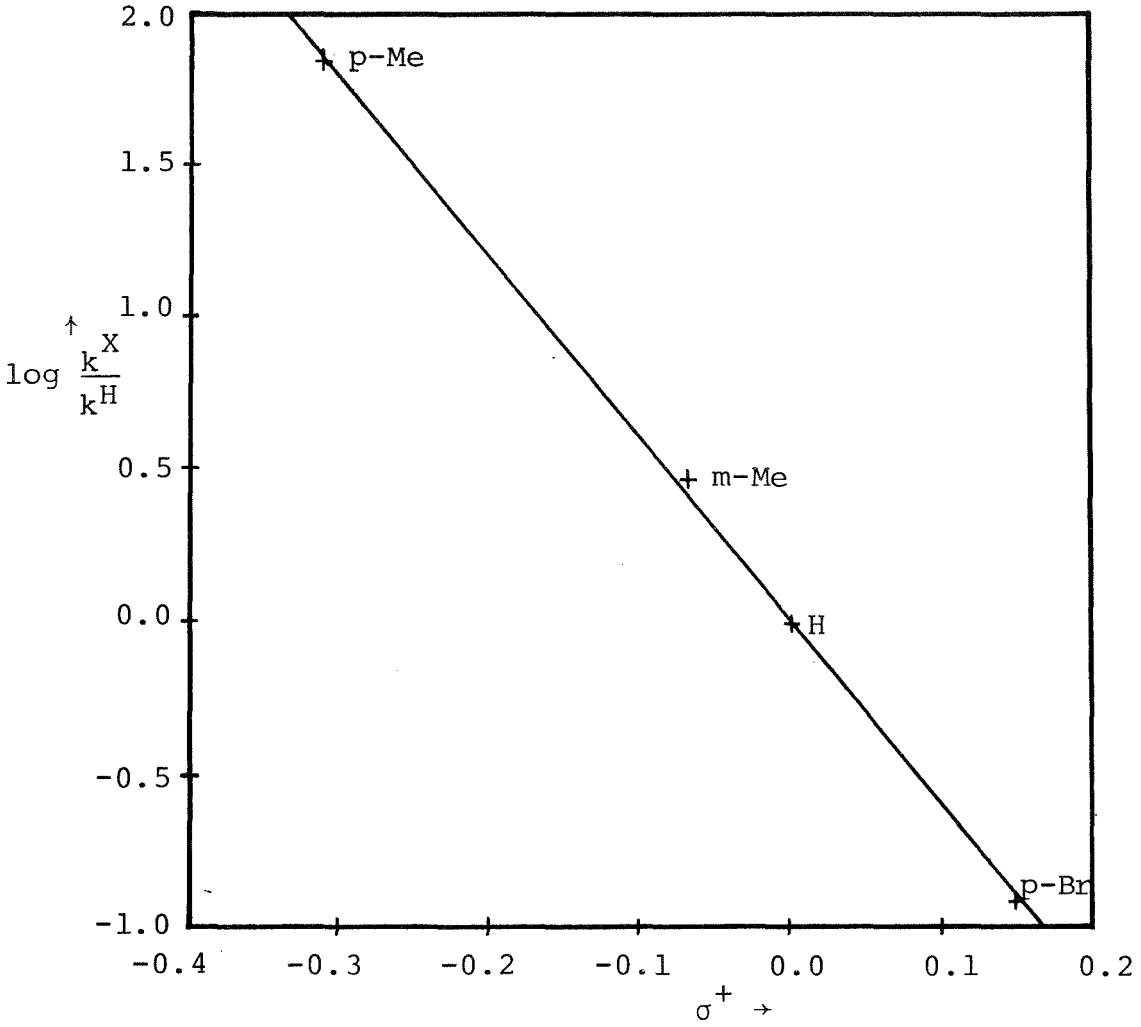


Table VI

Values of σ_p^+ for substituents not used to define ρ.

The relevant parameters for the Hammett correlation are:

Reaction constant,	ρ = -5.99
Intercept,	$\log k^H$ = +0.001
Correlation coefficient,	r = 0.9997
	SD/RMS = 0.028

Substituent	σ_p^+	
C_6H_5-N=N-	+0.09	(±0.01)
C_6H_5-N(O)=N-	-0.04	(±<0.01)
3-Cl-C_6H_4-N=N-	+0.15	(±0.02)
3-Br-C_6H_4-N=N-	+0.17	(±0.02)
4-F-C_6H_4-N=N-	+0.10	(±0.01)

Table VII

Previously reported literature values of σ_p^+ for the phenylazo substituent.

Method	σ_p^+
NBS,[a] C_6H_6, 80°	-0.15
HNO_3[b] Ac_2O, 0°	-0.19
Cl_2[c] HOAc, 25°	~-0.11
Diazonium coupling[d]	-0.37

a. Competitive side-chain bromination of toluenes.[8]

b. Competitive nitration.[7]

c. Kinetics of chlorination.[5] No product isomer ratios were reported. This σ_p^+ value is approximate, based on literature ρ values[2,29] together with an assumed ortho/para ratio of 1:1.

d. Value calculated by Hashida and co-workers[10] based on rates of diazonium coupling with R-acid at 20° and extrapolation using the Yukawa- Tsuno equation.[12]

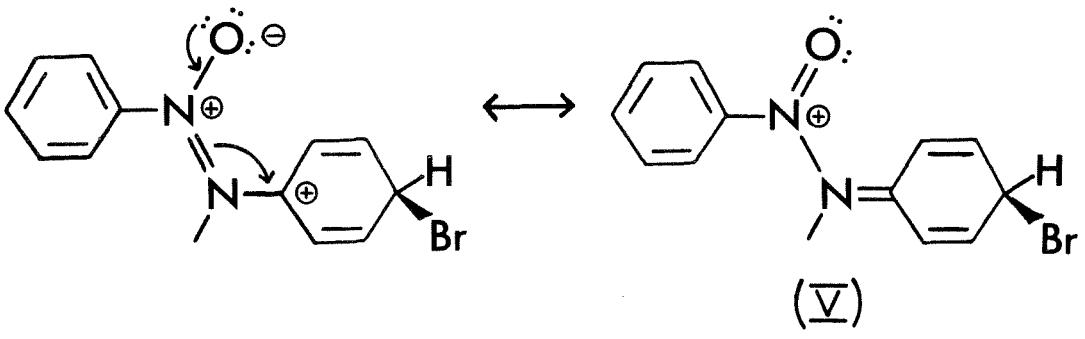
All the σ_p^+ values reported are consistent with the phenylazo group being ortho/para-directing and activating relative to benzene, whereas the present data, while confirming the ortho/para-directing nature of the substituent, show that it is deactivating. Although the conditions used in making these measurements should lead to a more reliable value than those previously reported, the discrepancy is too large to be accounted for in terms of experimental error alone. This applies especially to the chlorination data. The system used in this work differs from that used in the chlorination

study, because it is free from halide ions. This may be important with regard to any possible abnormality in the substitution process (as discussed by Robertson and co-workers[6]) or in the electrophile itself. A second difference is that the electrophile used in this study is much stronger than that used in the chlorination or nitration studies. The possible significance of this is discussed in the next section.

The electronic effect of the 4-fluorophenylazo substituent was found to be very similar to that of phenylazo, but as would be expected from the known σ_m values of the chloro and bromo substituents, the two 3-halogenophenylazo groups are more deactivating. As mentioned earlier, this deactivation was large enough to cause problems due to competing bromination in the already substituted ring. However, if the estimated k_3^{para} values for these two compounds are accepted as correct, then they lead to a value for the transmission coefficient of the 4-azophenylene linkage (π'_p) of about 0.20 for positive bromination. This figure is consistent with other reported values for this linkage,[4d] including that obtained in Part II of this thesis. Applying this π'_p value to k_3^{para} for 4-fluoroazobenzene, gives an apparent σ value of +0.05 for the p-fluoro substituent. This is approximately the same as that obtained from benzoic acid ionization, and suggests that the +R effect of this substituent plays a part in stabilising the Wheland intermediate for the substitution process, but

a considerably smaller one than when it is directly attached to the ring ($\sigma_{p\text{-}F}^{+} = -0.07$).[2] In a similar way, k_3^{ortho} values for azobenzene, 3-chloro- and 3-bromoazobenzene lead to a π'_o value of about 0.25 with an apparent σ value for the p-fluoro substituent of +0.02. The higher π' value (compared to that applying to the para-position) has already been rationalised in the previous section (p. 34), in terms of the greater inductive effect felt at the ortho-position. A greater resonance-induced inductive effect could also result in a more negative σ value for the p-fluoro substituent. The steric effects for ortho-attack on all substituted azobenzenes should be very similar.

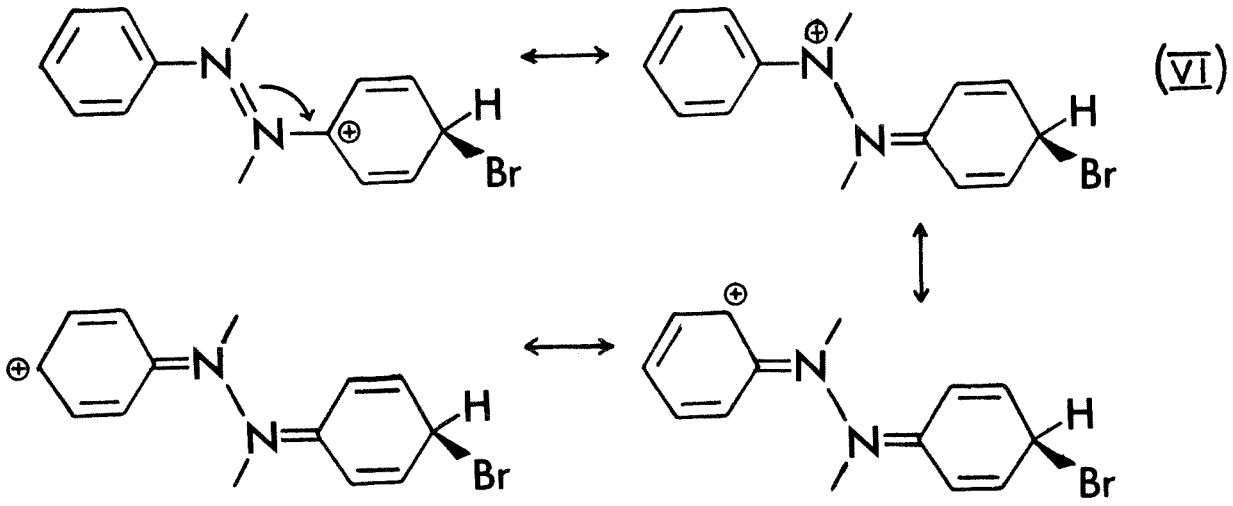
The negative value of σ_p^{+} obtained for the phenyl-ONN-azoxy substituent deserves comment. In spite of the expected increase in σ_I caused by the introduction of the oxygen, σ_p^{+} has decreased substantially, i.e. an increase in the rate of attack has resulted. This means that the value of σ_R^{+} has decreased so as to more than compensate for the increase in σ_I. This is interpreted as being due to the existence of the extra resonance form (V) which has no equivalent in the case of azobenzene.



(V)

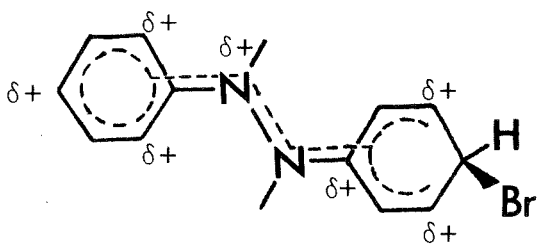
Mechanism of Stabilisation of Wheland Intermediates by Arylazo Substituents.

The magnitude of the various σ_p^+ values obtained for electrophilic substitution in azobenzene all require that the phenylazo group stabilize the Wheland intermediate (or, more accurately, lower the energy of the transition state leading to it) by some form of resonance interaction. This interaction may involve either the π-bond of the azo group or the lone pair of electrons on the nitrogen adjacent to the ring undergoing substitution. The two mechanisms of stabilisation are geometrically mutually exclusive. In the first case, the azo group and the reacting ring must be coplanar.

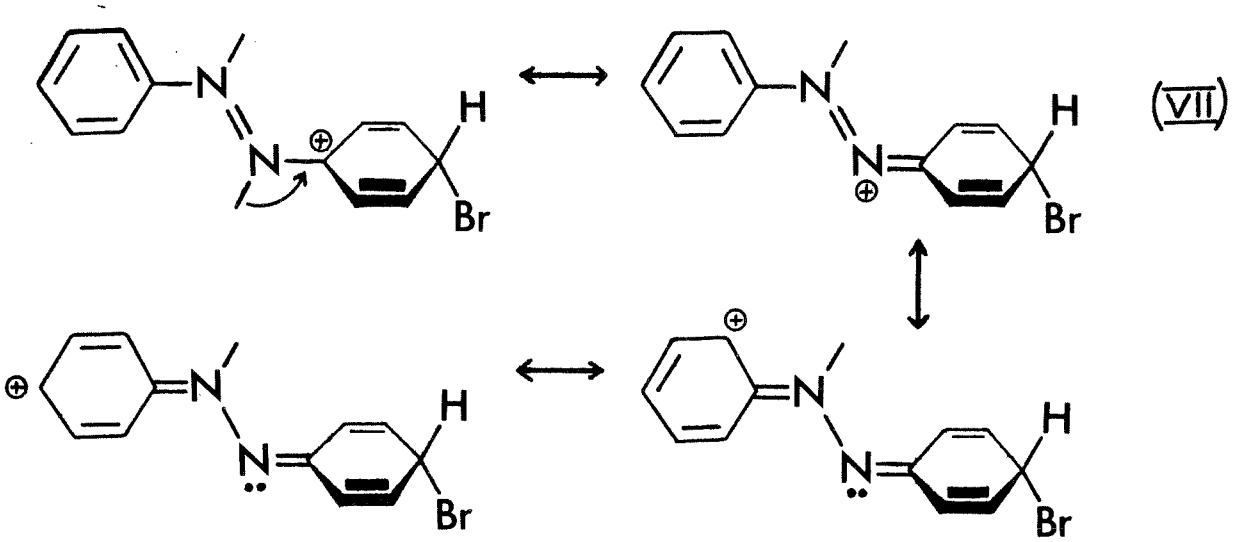


(VI)

Overall planar structure:

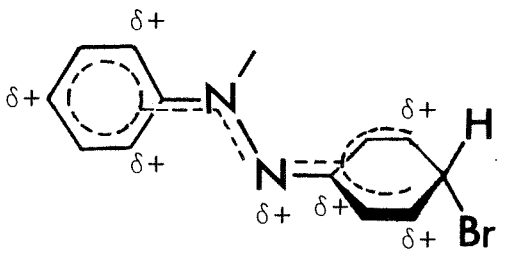


That the other ring must also lie in this plane is suggested by the fluoroazobenzene data, which require that the resonance effect of the F partly stabilise the Wheland intermediate. Furthermore structure (VI) with a nitrogen sextet, is, on its own, unlikely to be a major contributor; (the relative instability of forms containing the $>\overset{+}{N}-$ system is commonly invoked to explain the meta-directing influence of the aza substituent in pyridine[38]). In contrast, the alternative intermediate requires the azo group and the reacting ring to be orthogonal.



(VII)

Overall orthogonal structure:



It may be noted that all the structures except (VII) require that the non-reacting ring be coplanar with the azo group, a condition imposed on the basis of the evidence of the extent of +R interaction which is exerted in the case of 4-fluoroazobenzene (discussed previously). Since no electron-deficient nitrogen is involved, these three resonance forms may not be as important as in the fully coplanar case.

It was mentioned earlier that the σ_p^+ value obtained for azoxybenzene could only be accounted for by assuming participation by the lone pairs of the oxygen in resonance stabilisation of the intermediate (structure V). This implies coplanarity of the attacked ring with the azoxy group. Conversely, the ortho/para-directing nature of the nitroso group[39] (in contrast to the well known meta-directing behaviour of the isoelectronic nitro and formyl groups) can only be accounted for by assuming participation of the nitrogen lone pair, which implies non-coplanarity of the nitroso group and benzene ring in the transition state. This means that either type of resonance stabilisation, (VI) or (VII) can potentially take place in such systems, which makes it difficult to predict the likely situation for azobenzene since both predict the same result - that azobenzene be ortho/para-directing in electrophilic substitution.

Trans-azobenzene itself is known to exist as a planar molecule in the solid state.[40] In solution, free rotation is possible about the C-N bonds while still preserving the trans-orientation with respect to the azo group. In the case of the two structures proposed for

the Wheland intermediate, it is possible that they also interconvert very rapidly under the reaction conditions since only a 90^{o} rotation around a C-N bond is required, even though the energy barrier to rotation will be higher than is the case for non-reacting azobenzene.

The data for the halogenoazobenzenes also show that resonance interaction of some form does exist, and this can be of either type (VI) or (VII) proposed for azobenzene. Possibly of greater significance is the higher σ_p^+ observed for the phenylazo group in positive bromination when compared to substitutions involving weaker electrophiles. Whether bromination occurs by means of a preformed solvated "Br^+" species[13] or by means of protonation of a preformed association complex, HOBr.ArH, as postulated more recently,[41] it is clear that the effective electrophile is more reactive and also less selective than those used in nitration and other halogenation reactions. Therefore, according to the Hammond postulate,[42] the transition state would be more reactant-like. This could explain the source of the discrepancies in σ_p^+ values obtained for the phenylazo group. Azobenzene exists in solution as a mixture of conformers, of which the planar one can reasonably be expected to be of lower energy and therefore to predominate. A highly reactive electrophile would be capable of attacking any form, and the resulting reactant-like transition state would be mostly planar. The resulting intermediate may possibly be more stable in the non-planar configuration,

but since any subsequent change occurs after the rate determining step, this would not influence the rate of reaction. A less reactive electrophile might be expected to exhibit greater selectivity and a non-planar transition state might be preferred. The rate determining step would now be the formation of specifically this preferred non-planar transition state. The reactivity of the substrate would appear to be greater than in the former case, as indicated by its σ_p^+ value, even though the overall rate of reaction would be lower. In other words, the reaction rate of benzene (and other substituted benzenes used to define the Hammett plot) would be affected far more than that of azobenzene, upon changing the electrophile.

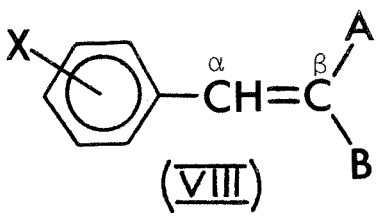
PART II

^{13}C N.M.R. STUDIES ON ETHYL CINNAMATES AND AZOBENZENES

INTRODUCTION

During the interpretation of results obtained in Part I, it was found necessary to determine the value of the transmission coefficient for the 3-azophenylene linkage. This coefficient, π', is the ratio of the reaction constants, ρ, obtained in the same reaction with and without the linkage (see Part I). Another interesting feature is the effect of the interposed linkage on the degree of direct resonance interaction between para-substituents and the reaction site. As mentioned in Part I, this shows up as differences in the σ values obtained for these substituents, with and without the linking group.

An important factor controlling the value of ρ is the distance between the substituent and the reaction site - the greater the distance, the smaller the reaction constant. Unfortunately, the experimental uncertainty does not decrease with ρ, so it becomes difficult to ascertain whether the changes observed are actually significant. On the other hand, measurements of physical properties can often be obtained more accurately than is the case with equilibrium or reactivity data. Currently, the most useful techniques available are measurements of ^{19}F and ^{13}C N.M.R. chemical shifts. It has recently been shown[43] that the ^{13}C N.M.R. chemical shifts of the β-carbon of ring-substituted styrene derivatives (VIII) can



(VIII)

(A,B constant)

be correlated by means of the Hammett equation. This implies that differences in chemical shift accompanying a change in substituent reflect a change in electron density at the β-carbon. The change in chemical shift caused by the substituent when compared to that of the parent compound is conveniently referred to as the substituent chemical shift (SCS), and is considered positive for downfield shifts.

The series of compounds chosen for study were the trans-β-carboethoxystyrenes, or ethyl cinnamates. These compounds are prepared relatively easily and are stable, whereas many styrenes polymerise on standing. Another advantage is that the moderate -R nature of the β-substituent enables quite strong resonance interaction to take place with +R para-substituents, while at the same time allowing interaction with -R ones as well (because of the ±R nature of the ethenyl group). Finally, the resonance of the β-carbon is sufficiently distant from those of the aromatic carbons to allow its unambiguous identification. A series of meta- and para-substituted ethyl cinnamates was prepared to obtain ρ for the aryl system (no interposed linkage). In order to determine the required transmission coefficient, a series of similarly substituted ethyl 3-arylazocinnamates was also prepared.

A literature survey of transmission coefficients for the 4-azophenylene linkage[4d] shows that variations occur according to the extent of interaction between the azo group and the side-chain in the system used. For this reason, it was

decided to use the same method to determine π' for the 4-azophenylene linkage, in order to compare it with that obtained in Part I. In addition, it would be of interest to compare this transmission coefficient with that of a system having carbon atoms in place of azo nitrogens. Two further series of ethyl 4-arylazocinnamates and ethyl 4-arylethenylcinnamates were prepared, and the ^{13}C N.M.R. spectra of all four series of compounds were determined under similar conditions.

Since the chemical shifts of most other carbon atoms were incidentally determined (in addition to the β-carbon atom), these were also examined to see if they could be correlated by the Hammett equation or extensions of it. To facilitate comparisons of ring-carbon data, two further series were used: meta- and para-substituted stilbenes[44] and azobenzenes.

EXPERIMENTAL

For column chromatography, Laporte Type H 100-200 mesh alumina was used. It was found to vary in activity from batch to batch, and in some cases was deactivated with water as required. Thin layer chromatography was carried out on T.L.C. grade alumina, eluting with benzene and developing in iodine vapour. Benzene and petroleum ether were technical grade, distilled from phosphorus pentoxide before use. Petroleum ether refers to the fraction of b.p. 50-70°, although during distillation, most of it was found to boil in the range 66-68°.

The ethanol used as a solvent for the preparation of the arylethenylcinnamates, was dried by refluxing over sodium and diethyl phthalate,[45] followed by distillation.

Carbon-13 N.M.R. spectra were obtained on a Varian CFT-20 N.M.R. spectrometer at a probe temperature of approximately 35°. Spectra were determined for solutions of 0.4M or less in deuterochloroform, with tetramethylsilane as internal standard. In all cases, only one isomer (presumably the trans,trans-isomer) was observed. In one case (ethyl 3-nitrosocinnamate) a specific proton decoupled spectrum was obtained to facilitate the assignment of the β-carbon.

Micro-analyses were carried out at the University of Otago.

All melting points are uncorrected.

(A) Preparation of Precursors.

(1) Anilines. All anilines used were commercially available and were used without further purification.

(2) Aldehydes. Eleven of the aldehydes used were obtained commercially and used without further purification. The preparation of the other two (3-fluoro and 4-bromo) is described below.

4-Bromobenzaldehyde.

This was prepared from 4-bromotoluene by Wohl-Ziegler bromination[46] followed by a Sommelet Reaction.[47]

A mixture of 34.2 g (0.20 mol) 4-bromotoluene, 35.8 g (0.20 mol) N-bromosuccinimide, and 6.9 g (0.020 mol) 70% benzoyl peroxide in 160 ml carbon tetrachloride was refluxed until no more solid N-bromosuccinimide remained on the bottom of the flask (approximately 45 minutes). The mixture was cooled externally with ice and the succinimide residues were filtered off and washed with carbon tetrachloride. The combined filtrates were washed once with dilute sodium carbonate solution and twice with water. After drying with anhydrous magnesium sulphate, the carbon tetrachloride was removed under reduced pressure. A white crystalline solid was obtained. This was dissolved in 30 ml chloroform and added to a solution of 31.0 g (0.22 mol) hexamine in 250 ml chloroform and refluxed with stirring for 3½ hours. It was then cooled externally with ice, the product filtered off, and washed twice with a small volume of cold chloroform. After drying in air, 50.5 g (65%, based on 4-bromotoluene) of the white crystalline hexaminium salt were obtained. This was refluxed in 120 ml of 50% v/v aqueous acetic acid for 2 hours. After cooling slightly, it was poured slowly with stirring into 400 ml cold water. The white crystalline precipitate was filtered off and washed with water,

dilute sodium carbonate solution, and water. After drying in air, the weight of product was 17.5 g (73%, based on hexaminium salt). This was used for the preparation of the corresponding arylethenylcinnamate without further purification.

3-Fluorobenzaldehyde

This was prepared by a similar method to the above compound. A mixture of 20.35 g (0.185 mol) 3-fluorotoluene, 33.0 g (0.185 mol) N-bromosuccinimide, and 6.4 g (0.0185 mol) 70% benzoyl peroxide in 150 ml carbon tetrachloride was heated under reflux. After a few minutes, the reaction became very vigorous and heating was ceased. After the reaction had subsided somewhat, heating was continued for half an hour, by which time no solid remained on the bottom of the flask. The same work-up procedure as above was used and a pale yellow liquid was obtained. This liquid was added to 28.0 g (0.20 mol) hexamine dissolved in 220 ml chloroform, and after refluxing with stirring for 4 hours, it was cooled (ice bath), filtered, and washed twice with chloroform. After drying in air, 37.6 g (62%, based on 3-fluorotoluene) of the white crystalline hexaminium salt were obtained. This was refluxed for 2 hours in 100 ml of 50% v/v aqueous acetic acid, cooled, and poured into 120 ml water. The oil obtained was extracted twice into ether, and the combined ether extracts were washed with water (once), dilute sodium carbonate solution (twice) and again with water (twice). Magnesium sulphate was used to dry the solution, and the ether was then removed under reduced pressure. A pale yellow oil was obtained (10.2 g, 72%, based on hexaminium

salt), which was used for the preparation of the corresponding arylethenylcinnamate and cinnamic acid without further purification.

(3) Cinnamic Acids.

A number of these were available in the department, having been used for previous studies. The others were prepared as described below.

3-Nitrocinnamic acid.[19b]

3-Nitrobenzaldehyde (50.0 g, 0.33 mol) and malonic acid (75.0 g, 0.72 mol) were dissolved in 150 ml pyridine containing 2.5 ml piperidine. This was heated on a steam bath for one hour, then refluxed for 5 minutes. After cooling, it was poured with stirring into 1.2 ℓ water containing 200 ml concentrated hydrochloric acid. The precipitate was filtered off, washed with water (three times), and dried in air, then in the oven. An off-white lumpy powder was obtained; yield: 55.2 g (86%). Recrystallisation of 1.0 g from ethanol gave 0.53 g off-white needles, m.p. 203-204^{o} (lit. 204.5-205.5^{o}).[48] The remainder was esterified without further purification.

4-Nitrocinnamic acid.

Exactly the same method was used as for the 3-isomer. A pale brown lumpy powder was obtained; yield: 57.9 g (91%). Recrystallisation of 1.0 g from ethanol gave 0.60 g off-white flakes, m.p. 286-287^{o} (lit. 287^{o}).[49]

3-Fluorocinnamic acid.

A mixture of pyridine (10 ml), piperidine (0.5 ml), 3-fluorobenzaldehyde (2.0 g, 0.016 mol) and malonic acid

(3.6 g, 0.035 mol) was heated on a steam bath for 2 hours, and then refluxed for 15 minutes. After cooling, the mixture was poured with stirring into 100 ml water containing 20 ml concentrated hydrochloric acid. This was filtered, washed once with dilute hydrochloric acid, twice with water, and finally air-dried. Yield: 2.1 g or 78%, white lumpy powder. The acid was esterified without further purification.

4-Fluorocinnamic acid.

The same method as above was used, yielding 2.3 g (86%) of this compound, as a white lumpy powder.

4-Methylcinnamic acid.

The same method was used as for the preparation of the nitrocinnamic acids, starting with 40.0 g (0.33 mol) of 4-methylbenzaldehyde with a heating period of 4 hours and a refluxing period of half an hour. A white powder was obtained; yield: 47.3 g (88%). One gram was recrystallised from alcohol, giving 0.56 g white flakes, m.p. 201.5 - 202°, (lit. 198°).[19b]

(B) Ethyl Cinnamates. (Not including arylazo- or arylethenyl-cinnamates.)

Ethyl Cinnamate.

This compound was available commercially.

Ethyl 3-nitrocinnamate.

To 54.2 g (0.281 mol) of the crude acid, 550 ml absolute alcohol and 30 ml concentrated sulphuric acid were added and refluxed for 4 hrs. After cooling this was poured into 1 ℓ water and a solution of 80 g anhydrous sodium carbonate in

300 ml water was added very carefully, with constant stirring. The product was then filtered off, washed three times with water, and dried in air. Yield: 58.2 g (94%) of off-white powder. Recrystallisation of 1.0 g from alcohol gave 0.63 g, long white needles, m.p. 75° (lit. 78-79°).[50]

Ethyl 4-nitrocinnamate.

The same method as above was used on 56.9 g (0.295 mol) of 4-nitrocinnamic acid. The yield was 61.1 g (94%) of the ester, as a pale brown powder. One gram was recrystallised from alcohol, giving 0.79 g pale brown needles, m.p. 139° (lit. 141-2°).[50]

Ethyl 3-nitrosocinnamate; (attempted preparation, using the method of Alway and Bonner[50]).

To 5.0 g (0.023 mol) ethyl 3-nitrocinnamate in 75 ml absolute alcohol and 12 ml glacial acetic acid, 3.3 g (0.046 mol) 90% zinc powder was added with vigorous stirring. The mixture did not warm up noticeably, so it was heated gently for 10 minutes, during which it turned green, then yellow-brown. The zinc residues were filtered off and washed with a small volume of hot ethanol. The combined filtrate and washings were then poured into a previously prepared and filtered solution of 8.0 g (0.049 mol) anhydrous ferric chloride in 80 ml water and 20 ml concentrated hydrochloric acid. A brown tar was formed, which was left for 10 minutes with occasional stirring. The mixture was then cooled by the addition of crushed ice and left for one hour, during which time the tar solidified to yellow-green crystals which were filtered off and washed with water. These crystals turned brown on storage

under refrigeration. Without further purification, the crude product was coupled to two anilines (3-chloro and 3-nitro) in glacial acetic acid as solvent, and the products purified by column chromatography on alumina. The ^{13}C N.M.R. spectra of the orange fractions showed that over 80% of them was unreacted ethyl 3-nitrocinnamate. A ^{13}C N.M.R. spectrum of the dried "nitroso-compound" showed mainly ethyl 3-nitrocinnamate peaks, together with other unidentified peaks, but no peaks identifiable as ethyl 3-nitrosocinnamate, when compared with the spectrum of a sample prepared later by a different method.

Ethyl 3-nitrosocinnamate.

An adaptation of the method of Lutz and Lytton[20] for the preparation of a large number of substituted nitroso compounds was used.

A solution of 10.0 g (0.045 mol) ethyl m-nitrocinnamate in 100 ml ethanol containing 15 ml water and 1.0 g calcium chloride dihydrate was refluxed, and 8.2 g (0.113 mol) 90% zinc powder added slowly with vigorous stirring. Refluxing and stirring were continued for a further 20 minutes, after which the zinc residues were filtered off and washed with hot alcohol. The orange filtrate and washings (combined) were then poured slowly with stirring into a previously prepared and filtered solution containing 16.0 g (0.099 mol) anhydrous ferric chloride in 50 ml concentrated hydrochloric acid, 350 ml water and 200 g crushed ice. A bright green solid was immediately obtained. The mixture was left for one hour with

occasional stirring, and after the ice had melted the product was filtered off and washed with water. After thorough drying on the filter, it was air-dried overnight under refrigeration and stored in the freezer under nitrogen. The ^{13}C N.M.R. spectrum of the crude material showed that there was still a considerable amount of starting material present together with the required product. For the purpose of coupling with anilines, the compound was used crude, but attempts were made to purify it in order to obtain a good ^{13}C N.M.R. spectrum. Steam distillation was found to be unsatisfactory owing to the similar volatility of the major impurity, the starting material. However, column chromatography proved satisfactory. Benzene (50 ml) was added to an undetermined amount of crude, wet compound which had been stored in the freezer. After shaking vigorously to dissolve as much compound as possible, a large amount of anhydrous magnesium sulphate was added, and it was left overnight. It was then filtered, most of the benzene removed, and after first carrying out a thin layer chromatogram, it was passed through 60 g alumina, using first 100 ml 20% benzene/petroleum ether and then 150 ml 35% benzene/petroleum ether to elute. A blue-green fraction was collected and yielded green crystals. The ^{13}C N.M.R. spectrum showed that it was about 75% pure. Further purification was not attempted.

Ethyl 4-nitrosocinnamate.

The same method was used as for the 3-isomer. Difficulty was experienced during the filtering off of the zinc residues because of a lower solubility of the arylhydroxylamine.

The sintered glass funnel became clogged and gravity filtration proved best, using fluted filter paper with the solution and glassware as hot as possible. After washing the residues with hot ethanol, the combined filtrate and washings were warmed to redissolve the precipitated arylhydroxylamine before adding to the ferric chloride solution. A lumpy yellow solid was obtained, which was very difficult to dry. It was used crude in large excess for coupling to anilines, and stored in the freezer under nitrogen. Again, steam distillation proved unsatisfactory, but column chromatography using the same method as for the 3-isomer gave a yellow solid which was more than 95% pure according to its ^{13}C N.M.R. spectrum.

Ethyl 4-methylcinnamate.

A mixture of 46.3 g (0.285 mol) 4-methylcinnamic acid, 350 ml ethanol, and 25 ml concentrated sulphuric acid was refluxed for 4 hours, and then most of the alcohol was distilled off. After cooling, the dark brown mixture was taken up in 200 ml ether and washed with water (once), dilute sodium carbonate solution (twice), and again with water (three times). It was then dried over magnesium sulphate, decolourised with charcoal, filtered, and the ether removed under reduced pressure. A brown oil was obtained; yield: 48.9 g (90%).

Ethyl 4-bromomethylcinnamate.[46]

Ethyl 4-methylcinnamate (46.7 g, 0.245 mol), N-bromosuccinimide (43.8 g, 0.246 mol) and 70% benzoyl peroxide (8.5 g, 0.025 mol) were refluxed in 200 ml carbon tetrachloride for 50 minutes, after which time the solid no longer sank to the bottom of the mixture. After cooling externally with ice, the succinimide residues were filtered off and washed with cold carbon tetrachloride. The filtrate and washings (combined) were washed with dilute sodium carbonate solution (once), water (twice), and dried with magnesium sulphate. Removal of the solvent under reduced pressure gave an orange-brown oil. This oil was impure and gave an apparent yield of over 100%. However, its ^{1}H N.M.R. spectrum showed that it was the desired product, containing about 20% starting material. It was used without further purification for the preparation of the phosphonium salt.

4-(2-Carboethoxyethenyl)benzyltriphenylphosphonium bromide.

This salt was prepared by the method used by Campbell and McDonald[51] for the preparation of 4-carbomethoxybenzyltriphenylphosphonium chloride.

Xylene (500 ml) and triphenylphosphine (64.4 g, 0.246 mol) were added to the product from the above reaction. After refluxing for 24 hours with stirring, the resulting fawn-coloured precipitate was filtered off and washed once with xylene, once with toluene, and twice with ether. After drying, 94.2 g (90%) of product was obtained. It was not purified further.

Other Ethyl Cinnamates

Other ethyl cinnamates required were prepared by the following general method: The cinnamic acid was refluxed in 10 ml of absolute alcohol containing 1 ml of concentrated sulphuric acid. After 3 hours the condenser was removed and most of the alcohol evaporated off. The resulting oil was taken up in 30 ml ether and washed once with water, twice with sodium carbonate solution, twice with water, dried over magnesium sulphate, and the ether evaporated. No further purification was necessary for the purposes of obtaining a ^{13}C N.M.R. spectrum. All the substituted ethyl cinnamates studied were known compounds.

Substituent	Wt acid used	Yield	Physical Appearance
3-Me	0.34g	0.28g (70%)	Pale yellow oil
3-F	0.50g	0.53g (91%)	Pale yellow oil
4-F	0.50g	0.55g (94%)	Off-white crystalline solid
3-Cl	0.50g	0.50g (87%)	Off-white crystalline solid
4-Cl	0.50g	0.52g (90%)	Very pale yellow oil
3-Br	0.50g	0.50g (89%)	Off-white crystalline solid
4-Br	0.50g	0.52g (93%)	Very pale yellow oil
4-OMe	0.50g	0.50g (86%)	Pale brown crystalline solid
4-NMe_2*	0.44g	0.43g (85%)	Yellow crystalline solid

*This was esterified as above, but before extraction into ether, the product was neutralized carefully with sodium carbonate solution until no more effervescence occurred. It was then taken up in ether, washed once with sodium carbonate solution and twice with water. The remainder of the procedure was as for the others.

(C) Ethyl 3-arylazocinnamates

The method shown below for ethyl 3-phenylazocinnamate was also adopted for all other 3-arylazocinnamtes except for the 4-N,N-dimethylamino compound. Reflux times varied from

5 to 40 minutes, depending on the basicity of the aniline used, and in the case of the 4-nitro-compound, a different solvent was used. Any other significant changes in the established procedure have been noted.

Ethyl 3-phenylazocinnamate.

Aniline (0.44 g, 4.7 mmol) was dissolved in 40 ml ethanol; 1.0 g crude, wet ethyl 3-nitrosocinnamate and 4.0g trichloroacetic acid were added, the solution was refluxed for 10 minutes and left overnight. The alcohol was then carefully removed under reduced pressure, and the residue taken up in 50 ml benzene. This solution was washed twice with dilute sodium carbonate, twice with water, and dried over magnesium sulphate. Most of the benzene was removed (2-3 ml remaining), and the compound was purified by column chromatography on 55 g alumina, eluting initially with petroleum ether, and then adding first 20%, and then 40% benzene, as required. The orange fraction gave 0.32 g (24%, based on aniline) of an orange crystalline solid. The ^{13}C N.M.R. spectrum showed that it contained a small amount of ethyl 3-nitrocinnamate. After dissolving in the minimum volume of benzene, chromatography was repeated on 18 g alumina, using petroleum ether with increasing concentrations of benzene to elute. Finally, recrystallisation from petroleum ether yielded long bright orange prisms, melting at 62.5°. Analysis: C,72.77; H,5.85; N,10.14%. $C_{17}H_{16}N_2O_2$ requires C,72.84; H,5.75; N,9.99%.

Ethyl 3-(3-methylphenylazo)cinnamate.

0.51 g (4.8 mmol) of 3-methylaniline gave 0.17 g (12%) of reasonably pure product after the initial columning. Recolumning and recrystallisation from petroleum ether gave bright orange plates, m.p. 65.5°. Analysis: C,73.40; H,6.29; N,9.65%. $C_{18}H_{18}N_2O_2$ requires C,73.45; H,6.16; N,9.52%.

Ethyl 3-(4-methylphenylazo)cinnamate.

0.51 g (4.8 mmol) of 4-methylaniline gave 0.20 g (14%) of product. Further purification gave shiny orange flakes (petroleum ether), m.p. 76.5°. Analysis: C,73.55; H,6.04; N,9.68%. $C_{18}H_{18}N_2O_2$ requires C,73.45; H, 6.16; N,9.52%.

Ethyl 3-(3-fluorophenylazo)cinnamate.

0.53 g (4.8 mmol) of 3-fluoroaniline gave 0.44 g (31%) of slightly impure product. Further purification gave long bright orange needles (petroleum ether) which melted at 79°, but seemed to resolidify and remelt at 86°. Analysis: C,68.68; H,5.31; N,9.50%. $C_{17}H_{15}FN_2O_2$ requires C,68.45, H,5.07; N,9.39%.

Ethyl 3-(4-fluorophenylazo)cinnamate.

0.53 g (4.8 mmol) of 4-fluorotoluene gave 0.41 g (29%) of product; thin, shiny orange flakes (petroleum ether), m.p. 58°. Analysis: C,68.28; H,5.07; N,9.36%. $C_{17}H_{15}FN_2O_2$ requires C,68.45; H,5.07; N,9.39%.

Ethyl 3-(3-chlorophenylazo)cinnamate.

0.61 g (4.8 mmol) of 3-chloroaniline gave 0.17 g (11%) of product; fine, pale orange needles (petroleum ether), m.p. 58°. Analysis: C,65.01; H,4.98; N,8.98%. $C_{17}H_{15}ClN_2O_2$ requires C,64.87; H,4.80; N,8.90%.

Ethyl 3-(4-chlorophenylazo)cinnamate.

0.61 g (4.8 mmol) of 4-chloroaniline gave 0.31 g (21%) of product; a mixture of fine orange needles and flakes (petroleum ether). Two different melting points were observed: the needles melted at 90°, the flakes at 97°. Analysis: C,64.65; H,4.85; N,8.99%. $C_{17}H_{15}ClN_2O_2$ requires C,64.87; H,4.80; N,8.90%.

Ethyl 3-(3-bromophenylazo)cinnamate.

0.82 g (4.8 mmol) of 3-bromoaniline gave 0.58 g (34%) of impure product. Further purification gave fine orange needles (petroleum ether) which melted at 51°, resolidified, and remelted at 62°. Analysis: C,56.65; H,4.22; N,7.93%. $C_{17}H_{15}BrN_2O_2$ requires C,56.84; H,4.21; N,7.80%.

Ethyl 3-(4-bromophenylazo)cinnamate.

0.82 g (4.8 mmol) of 4-bromoaniline gave 0.79 g (46%) of very impure product. When repurified, this gave very fine orange flakes with a few needles (petroleum ether). Two melting points were observed: 97.5° (needles), and 98.5° (flakes). Analysis: C,57.23; H,4.27; N,7.56%. $C_{17}H_{15}BrN_2O_2$ requires C,56.84; H,4.21; N,7.80%.

Ethyl 3-(4-methoxyphenylazo)cinnamate.

0.59 g (4.8 mmol) of 4-methoxyaniline gave 0.30 g (20%) of a product whose ^{13}C N.M.R. spectrum showed that it contained roughly an equal amount of ethyl 3-nitrocinnamate. Thin layer chromatography showed that the two compounds have very similar r.f. values. Therefore, for the second purification, the compound was not put onto the column with benzene, but was

dissolved in ether, 2.5 g alumina were added, and the ether was allowed to slowly evaporate. The adsorbed compound was then put onto a column of 25 g alumina, and eluted very slowly with 200 ml 20% benzene and then 100 ml 25% benzene. Recrystallisation of the orange fraction from a relatively large volume of petroleum ether gave long pale yellow needles. These, from their melting point and infra-red spectrum, were identified as ethyl 3-nitrocinnamate. The mother liquor was allowed to evaporate slowly to dryness, and more pale-coloured needles were formed. These were picked out by hand from the thicker orange prisms which were also present. The latter were redissolved in hot petroleum ether, and upon seeding the solution, large bright orange prisms were formed, m.p. 64.5°. Analysis: C,69.39; H,5.86; N,8.76%. $C_{18}H_{18}N_2O_3$ requires C,69.66; H,5.85; N,9.03%.

Ethyl 3-(3-nitrophenylazo)cinnamate.

0.66 g (4.8 mmol) of 3-nitroaniline, after refluxing for 40 minutes, gave 0.32 g (21%) of a product which was mainly ethyl 3-nitrocinnamate, containing about 35% of the required product according to its ^{13}C N.M.R. spectrum. Thin layer chromatography showed that because of similar r.f. values, a careful separation was required. The product was dissolved in the minimum volume of ether, 2.5 g alumina were added, and the ether allowed to evaporate. This was put onto a column of 25 g alumina and eluted with 20% benzene (100 ml), 30% benzene (200 ml), and finally 35% benzene (100 ml).

Recrystallisation from a comparatively large volume of petroleum ether with slow cooling gave fine orange needles which formed in clusters, m.p. 119°. Analysis: C,62.75; H,4.70; N,12.74%. $C_{17}H_{15}N_3O_4$ requires C,62.76; H,4.65; N,12.92%.

Ethyl 3-(4-nitrophenylazo)cinnamate.

An attempt was made to prepare this compound by exactly the same procedures as the previous compound. However, the product obtained after one purification through alumina contained over 90% ethyl 3-nitrocinnamate, according to its ^{13}C N.M.R. spectrum. It was decided to attempt the coupling reaction in acetic acid/trichloroacetic acid,[52] and then to reflux in ethanol to ensure that the product was the ester and not the acid.

0.66 g (4.8 mmol) of 4-nitroaniline was dissolved in 30 ml glacial acetic acid; 1.0 g crude, wet ethyl 3-nitrosocinnamate and 5.0 g trichloroacetic acid were added. This was heated on a steam bath for 4 hours, then left overnight. The acetic acid was then removed under reduced pressure, 40 ml ethanol were added, and this was refluxed for one hour, cooled, and the alcohol carefully removed, again under reduced pressure. The residue was worked up and chromatographed in the usual manner. The bright orange fraction gave 0.21 g of product which according to its ^{13}C N.M.R. spectrum, was still only about 20% pure. The product was repurified on 18 g alumina, eluting more slowly this time, using first petroleum ether, then 10% benzene (100 ml) 20% benzene (200 ml), and finally 30% benzene. This time the yield of orange material was

74 mg (5%), and its ^{13}C N.M.R. spectrum showed that it was about 50% pure. Column chromatography was repeated for a third time. It was dissolved in the minimum volume of benzene, 1 g alumina was added, and the benzene allowed to evaporate. This was put onto a column containing 25 g alumina, and eluted with 20% benzene (100 ml), 40% benzene (100 ml) and finally 50% benzene. The orange fraction was recrystallised from a rather large volume of petroleum ether, and short dark red needles were obtained, which melted at 114°, then resolidified and melted at 120°. Analysis: C,62.63; H,4.77; N,12.90%. $C_{17}H_{15}N_3O_4$ requires C,62.76; H,4.65; N,12.92%.

Ethyl 3-(4-N,N-dimethylaminophenylazo)cinnamate.

This was prepared from ethyl 3-nitrocinnamate by reduction followed by diazotisation and diazonium coupling to N,N-dimethylaniline. Acetyl chloride (7 ml) was added slowly with stirring to absolute alcohol (50 ml). This was allowed to cool and 2.0 g (9.0 mmol) ethyl 3-nitrocinnamate were added and stirred until dissolved. Next 3.2 g (27.0 mmol) tin metal was added as a coarse powder, vigorous stirring being maintained. The reaction mixture became slightly warm. Gentle heating and vigorous stirring were continued for one hour, by which time the tin had all dissolved and about one half of the solvent had evaporated off. An ice-salt bath was used to cool the solution and 10 ml concentrated hydrochloric acid were added, followed by the slow addition, with stirring, of 0.70 g (10.1 mmol) sodium nitrite dissolved in 2 ml water.

Starch-iodide paper showed that the nitrite was in excess. Stirring was continued while 6.6 g sodium acetate was added followed by enough sodium carbonate to raise the pH to 3-4. Then a solution of 1.1 g (9.1 mmol) N,N-dimethylaniline in 5 ml ethanol was added. The mixture turned a bright orange, but slowly changed to a red colour. Sodium bicarbonate was added until the colour reverted back to orange. The mixture was then extracted twice with benzene and the extracts washed three times with water and dried over anhydrous potassium carbonate. Most of the solvent was then evaporated under reduced pressure, and the compound was chromatographed on 62 g alumina with 20% benzene as eluent. The orange fraction gave 0.62 g (21%) of product which showed no impurities in its ^{13}C N.M.R. spectrum. However, it was chromatographed again on 50 g alumina and recrystallised from petroleum ether, yielding short, bright orange needles, m.p. 113°. Analysis: C,70.88; H,6.64; N,13.34%. $C_{19}H_{21}N_3O_2$ requires C,70.57; H,6.55; N,12.99%.

(D) Ethyl 4-arylazocinnamates.

The method used for the preparation of these was basically the same as for the 3-arylazocinnamates. A larger excess of nitroso compound was used because it was much wetter than the 3-isomer. More trichloroacetic acid was used, the reflux times were increased slightly, and a wash with dilute hydrochloric acid was included, in order to remove any unreacted aniline. After the initial refluxing and cooling, a precipitate was

formed in all cases. Before the work-up, this precipitate was filtered off and found (by melting point, infra-red spectroscopy, and ^{13}C N.M.R. spectroscopy) to be neither the required product nor the starting material (ethyl 4-nitrocinnamate), so it was discarded. Furthermore, the precipitates obtained from preparations of different compounds in this series had identical infra-red spectra. It appears, therefore, that the precipitate originates from the nitroso compound. The detailed procedure is given for the unsubstituted compound and any significant changes in procedure for the others are noted.

Ethyl 4-phenylazocinnamate.

Aniline (0.44 g, 4.7 mmol) was dissolved in 40 ml ethanol, 3.0 g crude, wet ethyl 4-nitrosocinnamate and 5.0 g trichloroacetic acid were added; the solution was refluxed for 15 minutes and left overnight. The precipitate which formed was filtered off, the ethanol was carefully evaporated under reduced pressure and 50 ml benzene were added. The solution was washed once with dilute hydrochloric acid, twice with dilute sodium carbonate solution, three times with water, and dried over magnesium sulphate. Most of the benzene was then evaporated and the compound chromatographed on 55 g alumina, eluting initially with petroleum ether. The orange fraction slowed half-way down, and elution was completed with 100 ml of 20% benzene and then 100 ml of 30% benzene, yielding 0.17 g (13%, based on aniline) of an orange compound which contained about

10% ethyl 4-nitrocinnamate, according to its ^{13}C N.M.R. spectrum. It was redissolved in the minimum volume of benzene and chromatography was repeated on 18 g alumina, eluting with 10% benzene (50 ml), 20% benzene (50 ml), and then 25% benzene (90 ml). Finally, the orange fraction was recrystallised from petroleum ether, yielding orange-red plates, m.p. 102.5° (lit. 101-102°).[53]

Ethyl 4-(3-methylphenylazo)cinnamate.

0.51 g (4.8 mmol) of 3-methylaniline gave 94 mg (7%) of reasonably pure product after the initial columning. Recolumning followed by recrystallisation from petroleum ether gave short, thick, dark red prisms, m.p. 70°. Analysis: C,73.65; H,6.38; N,9.49%, $C_{18}H_{18}N_2O_2$ requires C,73.45; H,6.16; N,9.52%.

Ethyl 4-(4-methylphenylazo)cinnamate.

0.51 g (4.8 mmol) of 4-methylaniline gave 0.18 g (13%) of product. Further purification gave small bright orange plates (petroleum ether), m.p. 126°. Analysis: C,73.31; H,6.31; N,9.57%. $C_{18}H_{18}N_2O_2$ requires C,73.45; H,6.16; N,9.52%.

Ethyl 4-(3-fluorophenylazo)cinnamate.

0.53 g (4.8 mmol) of 3-fluoroaniline gave 0.17 g (12%) of product; large orange-red prisms (petroleum ether), m.p. 80.5°. Analysis: C,68.60; H,5.23; N,9.35%. $C_{17}H_{15}FN_2O_2$ requires C,68.45; H,5.07; N,9.39%.

Ethyl 4-(4-fluorophenylazo)cinnamate.

0.53 g (4.8 mmol) of 4-fluoroaniline gave 0.19 g (13%) of product; long, thin rectangular flakes (petroleum ether), glossy orange colour, m.p. 150°. Analysis: C,68.58; H,5.03; N,9.35%. $C_{17}H_{15}FN_2O_2$ requires C,68.45; H,5.07; N,9.39%.

Ethyl 4-(3-chlorophenylazo)cinnamate.

0.61 g (4.8 mmol) of 3-chloroaniline gave 0.21 g (14%) of slightly impure product. Further purification gave long fine orange needles (petroleum ether), m.p. 82°. If resolidified, it melted at 90°. Analysis: C,64.84; H,5.05; N,9.03%. $C_{17}H_{15}ClN_2O_2$ requires C,64.87; H,4.80; N,8.90%.

Ethyl 4-(4-chlorophenylazo)cinnamate.

0.61 g (4.8 mmol) of 4-chloroaniline gave 0.16 g (11%) of reasonably pure product. For solubility reasons, this was adsorbed onto alumina and the solvent evaporated, before being recolumned. Recrystallisation from petroleum ether gave bright orange needles which softened into a globule at 121° and melted to a clear liquid at 123°. After solidifying, it remelted at 124.5-125°. Analysis: C,64.50; H,4.96; N,8.83%. $C_{17}H_{15}ClN_2O_2$ requires C,64.87; H,4.80; N,8.90%.

Ethyl 4-(3-bromophenylazo)cinnamate.

0.82 g (4.8 mmol) of 3-bromoaniline gave 0.33 g (19%) of product; fine orange needles (petroleum ether). A small amount melted at 90.5°, but most melted at 100°.

Analysis: C,56.57; H,4.26; N,7.90%. $C_{17}H_{15}BrN_2O_2$ requires C,56.84; H,4.21; N,7.80%.

Ethyl 4-(4-bromophenylazo)cinnamate.

0.82 g (4.8 mmol) of 4-bromoaniline gave 0.20 g (12%) of product which was adsorbed onto alumina and recolumned. Recrystallisation from petroleum ether gave very fine orange needles. The melting point was not distinct and the analysis was not very satisfactory. The compound was therefore carefully recrystallised a second time, and larger bright orange needles were obtained. A small proportion of these melted at 112° and the rest at 124°. Upon solidifying and remelting, all melted at 124°. Analysis: C,57.23; H,4.38; N,7.76%. $C_{17}H_{15}BrN_2O_2$ requires C,56.84; H,4.21; N,7.80%.

Ethyl 4-(4-methoxyphenylazo)cinnamate.

0.59 g (4.8 mmol) of 4-methoxyaniline was used. Thin layer chromatography of the crude product showed that the r.f. value of the major impurity (ethyl 4-nitrocinnamate) was very similar to that of the azo compound, with the former coming through first. Therefore a longer column with 66 g alumina was prepared and the compound put onto the column with the minimum volume of benzene. Elution was carried out slowly, with up to 40% benzene at the end. A colourless fraction just before the orange one gave white needles which were identified (by melting point and infra-red spectrum) as ethyl 4-nitrocinnamate. The beginning of the orange fraction was discarded in order to exclude as much of the nitro compound as possible, and 0.23 g (15%) of orange product

was collected which still contained up to 30% of nitro compound. This product was dissolved in benzene, 1.2 g alumina were added, and after allowing the benzene to evaporate, it was columned again on 27 g alumina, eluting with up to 60% benzene. Recrystallisation from petroleum ether gave shiny orange flakes, m.p. 118.5° (indistinct). Analysis: C,69.50; H,6.14; N,9.00%. $C_{18}H_{18}N_2O_3$ requires C,69.66; H,5.85; N,9.03%.

Ethyl 4-(3-nitrophenylazo)cinnamate.

0.66 g (4.8 mmol) of 3-nitroaniline, 3.0 g of crude, wet nitroso compound and 7.0 g of trichloroacetic acid were refluxed in 40 ml ethanol for one hour and worked up in the usual way. Thin layer chromatography of the crude product showed that ethyl 4-nitrocinnamate came through first, closely followed by the azo compound. Therefore a column containing 75 g alumina was prepared, and after eluting with up to 50% benzene and discarding the first part of the orange fraction (to exclude as much ethyl 4-nitrocinnamate as possible), 0.13 g (8%) of pure (by ^{13}C N.M.R.) product was obtained. This product was columned again (after first adsorbing onto 1.5 g alumina) on 22 g alumina, eluting with up to 60% benzene. Recrystallisation from petroleum ether required a large volume (about 50 ml), and gave (after several days) red-orange plates, m.p. 149°. Analysis: C,62.43; H,4.82; H,12.73%. $C_{17}H_{15}N_3O_4$ requires C,62.76; H,4.65; N,12.92%.

Ethyl 4-(4-nitrophenylazo)cinnamate.

0.66 g (4.8 mmol) of 4-nitroaniline was dissolved in 40 ml glacial acetic acid; 5.0 g trichloroacetic acid and 3.0 g crude,

wet ethyl 4-nitrosocinnamate were added, and the mixture was heated on a steam bath for 4 hours and then left overnight. The pale yellow precipitate which formed was filtered off and the acetic acid was taken off under reduced pressure. The residue was refluxed for one hour in 40 ml ethanol and allowed to cool. More precipitate was formed, and this was also filtered off. The ethanol was carefully evaporated under reduced pressure, the residue was taken up in 60 ml benzene and washed and dried as usual. Thin layer chromatography of the residue showed that separation from ethyl 4-nitrocinnamate (which came through first) would be difficult, and a longer column with slow careful elution would be required. Accordingly, most of the benzene was removed and the compound was columned on 78 g alumina, increasing the proportion of benzene slowly up to 50%. The yield was 0.15 g (9%), and contained about 30% ethyl 4-nitrocinnamate, although it was difficult to estimate because the compound was not soluble to 0.4M in deuterochloroform. The compound was columned again on 27 g alumina (after first adsorbing onto 1.3 g alumina), eluting with up to 60% benzene. Finally, recrystallisation from about 50 ml petroleum ether gave short maroon-red needles, m.p. 178.5°. Analysis: C,62.49; H,4.77; N,12.67%. $C_{17}H_{15}N_3O_4$ requires C,62.76; H,4.65; N,12.92%.

Ethyl 4-(4-N,N-dimethylaminophenylazo)cinnamate.

The method was similar to that used for the 3,4-isomer. To 50 ml absolute alcohol, 7 ml acetyl chloride was added slowly with stirring and external cooling, followed by 2.0 g (9.0 mmol) ethyl 4-nitrocinnamate. The mixture was warmed gently until the compound had dissolved, and 3.2 g (27.0 mmol)

tin metal was added as a coarse powder. Vigorous stirring and gentle heating were maintained for one hour, during which time the tin had all dissolved, yielding a brownish solution, and the volume of solvent had approximately halved. The solution was cooled (ice-salt bath), which caused the amine to precipitate out, and 12 ml concentrated hydrochloric acid were added (the amine still did not dissolve). This was diazotised by the slow addition with stirring of 0.70 g (10.1 mmol) sodium nitrite in 2 ml water, which caused the precipitate to dissolve. After half an hour, 1.1 g (9.1 mmol) N,N-dimethylaniline in 5 ml ethanol was added with stirring followed by 6.6 g sodium acetate. At this stage the mixture had assumed a bright maroon-red colour. The addition of 5 g sodium carbonate brought the pH to 1-2. More sodium carbonate and sodium bicarbonate were carefully added as required until the pH was in the region of 5-6. At this stage the mixture had changed to a bright orange colour. After a further half hour of stirring, the mixture was extracted twice with benzene. The benzene extracts (dark brown-maroon in colour) were washed three times with water, dried over anhydrous potassium carbonate, and columned twice on alumina. The intense red fraction, which amounted to 50 mg (2%), was recrystallised from petroleum ether. The orange solution gave long dark-red needles, m.p. 157.5°. Analysis: C,70.26; H,6.61; N,13.12%. $C_{19}H_{21}N_3O_2$ requires C,70.57; H,6.55; N,12.99%.

(E) Ethyl 4-(2-arylethenyl)cinnamates.

This series of compounds was prepared by reacting the appropriate aldehyde with 4-(2-carboethoxyethenyl)benzyl-triphenylphosphonium bromide in super-dry ethanol in the presence of sodium ethoxide. A stock solution of sodium ethoxide containing slightly more than 0.173 g (7.5 mmol) sodium per 10 ml ethanol was prepared by scraping the oxide layer off a lump of sodium (kept under petroleum ether), weighing it into the calculated volume of dry alcohol, and allowing it to react in a flask protected from moist air.

After one week the products were filtered off from the reaction mixtures. Because of differences in solubility of the products, in some cases water was added just before filtration in order to make the product precipitate out or to increase the yield of precipitated product. If too much water was added, an impure oil resulted.

The method described for the unsubstituted compound was used for the preparation of all the others except the 4-nitro compound.

Ethyl 4-(2-phenylethenyl)cinnamate.

To 4.0 g (7.5 mmol) of the phosphonium salt, were added 0.85 g (8.0 mmol) benzaldehyde, 20 ml dry ethanol, and 10 ml dry sodium ethoxide solution. The dark brown colour of the ylide appeared and a suspension remained. This was left at room temperature for one week with occasional shaking. The solid was then filtered off, washed with a small volume of cold ethanol, and allowed to dry. The yield of crude product

was 0.35 g (17%) of a pale fawn-coloured lumpy powder. This was triturated several times with ether, the ether extracts were filtered, and the remaining solid discarded. Evaporation of the ether gave a white powder whose ^{13}C N.M.R. spectrum showed no signs of impurities. Some was recrystallised twice from petroleum ether (pale yellow flakes, m.p. 144°) and the remainder from ethanol (pale yellow-green plates, m.p. 144.5°). In solution and when melted, the compound was noticeably fluorescent with a green or pale blue tinge. The ethanol-recrystallised sample was analysed. Analysis: C,81.92; H,6.46%. $C_{19}H_{18}O_2$ requires C,81.99; H,6.52%.

Ethyl 4-[2-(3-methylphenyl)ethenyl]cinnamate.

0.92 g (7.7 mmol) of 3-methylbenzaldehyde, after adding 10 ml water, filtering, washing with 75% aqueous alcohol and drying, gave 0.53 g (24%) of a light, fluffy cream-coloured solid. The ether extract was recrystallised twice from alcohol, yielding pale yellow, light fluffy flakes and needles, m.p. 103.5°. Analysis: C,82.09; H,6.88%. $C_{20}H_{20}O_2$ requires C,82.16; H,6.89%.

Ethyl 4-[2-(4-methylphenyl)ethenyl]cinnamate.

0.92 g (7.7 mmol) of 4-methylbenzaldehyde gave, after dilution with 5 ml water, 0.53 g (24%) of product. Further purification gave extremely fine powdery needles (ethanol) pale green in colour, m.p. 206°. Analysis: C,82.16; H,7.12%. $C_{20}H_{20}O_2$ requires C,82.16; H,6.89%.

Ethyl 4-[2-(3-fluorophenyl)ethenyl]cinnamate.

0.98 g (7.9 mmol) of 3-fluorobenzaldehyde, after quenching with 15 ml water, gave 0.23 g (10%) of product; long thin rectangular flakes (ethanol), pale yellow in colour, m.p. 108°. Analysis: C,77.26; H,5.99%. $C_{19}H_{17}FO_2$ requires C,77.01; H,5.78%.

Ethyl 4-[2-(4-fluorophenyl)ethenyl]cinnamate.

0.95 g (7.7 mmol) of 4-fluorobenzaldehyde gave, after adding 10 ml water, 0.53 g (24%) of a tan-coloured crystalline mass, which gave after further purification, pale yellow flakes (ethanol), m.p. 152.5°. Analysis: C,76.87; H,5.99%. $C_{19}H_{17}FO_2$ requires C,77.01; H,5.78%.

Ethyl 4-[2-(3-chlorophenyl)ethenyl]cinnamate.

1.08 g (7.7 mmol) of 3-chlorobenzaldehyde, after the addition of 10 ml water, gave 0.45 g (19%) of a pale yellow crystalline solid, most of which was soluble in ether. Recrystallisation (twice) from ethanol gave very fine pale yellow needles, m.p. 94°. Analysis: C,73.25; H,5.64%. $C_{19}H_{17}ClO_2$ requires C,72.96; H,5.48%.

Ethyl 4-[2-(4-chlorophenyl)ethenyl]cinnamate.

1.06 g (7.5 mmol) of 4-chlorobenzaldehyde gave 0.44 g (19%) of product; shiny, pale yellow flakes (ethanol), m.p. 147°. Analysis: C,72.82; H,5.58%. $C_{19}H_{17}ClO_2$ requires C,72.96; H,5.48%.

Ethyl 4-[2-(3-bromophenyl)ethenyl]cinnamate.

1.42 g (7.7 mmol) of 3-bromobenzaldehyde, after adding 7 ml water gave 0.52 g (19%) of product; very fine creamy-yellow needles (ethanol), m.p. 100.5°. Analysis: C,63.73; H,4.71%. $C_{19}H_{17}BrO_2$ requires C,63.88; H,4.80%.

Ethyl 4-[2-(4-bromophenyl)ethenyl]cinnamate.

1.40 g (7.6 mmol) of 4-bromobenzaldehyde gave, after dilution with 5 ml water, 0.68 g (25%) of product; shiny pale creamy-yellow flakes (ethanol), m.p. 165.5°. Analysis: C,63.73; H,4.78% $C_{19}H_{17}BrO_2$ requires C,63.88; H,4.80%.

Ethyl 4-[2-(4-methoxyphenyl)ethenyl]cinnamate.

1.04 g (7.6 mmol) of 4-methoxybenzaldehyde gave 0.43 g (19%) of crude product. Trituration with ether (several times) gave a solution which was intensely fluorescent (pale blue). The product was recrystallised twice from ethanol, giving a mixture of very pale yellow-green flakes and needles which melted at 207° but seemed to solidify and melt again at 209° to a clear yellow liquid. Analysis: C,77.72; H,6.47%. $C_{20}H_{20}O_3$ requires C,77.90; H,6.54%.

Ethyl 4-[2-(4-N,N-dimethylaminophenyl)ethenyl]cinnamate.

1.13 g (7.6 mmol) of 4-N,N-dimethylaminobenzaldehyde resulted in a bright orange-yellow mixture which yielded 0.52 g (21%) of a bright yellow lumpy solid. After triturating several times with ether, a solution was obtained which appeared bright yellow in subdued light, but gave a very bright green fluorescence in strong light. After evaporation of the

ether, the product was recrystallised three times from alcohol. Bright yellow powdery crystals were obtained, whose crystalline form was difficult to determine. These softened slightly at 207-208^{o} and finally melted at 209-210^{o} to an orange-red liquid. Analysis: C,78.12; H,7.21; N,4.39%. $C_{21}H_{23}NO_2$ requires C,78.47; H,7.21; N,4.36%.

Ethyl 4-[2-(3-nitrophenyl)ethenyl]cinnamate.

1.14 g (7.5 mmol) of 3-nitrobenzaldehyde was dissolved by warming in 20 ml dry ethanol and the phosphonium salt and sodium ethoxide solution were then added, yielding 0.64 g (26%) of crude product. Further purification gave very fine yellow prisms (ethanol), m.p. 145.5^{o}. Analysis: C,70.42; H,5.42; N,4.32%. $C_{19}H_{17}NO_4$ requires C,70.58; H,5.30; N,4.33%.

Ethyl 4-[2-(4-nitrophenyl)ethenyl]cinnamate.

1.14 g (7.5 mmol) of 4-nitrobenzaldehyde was dissolved (with warming) in 15 ml commercial absolute alcohol. The phosphonium salt was added, followed by 15 ml of lithium ethoxide solution containing 0.052 g (7.5 mmol) lithium per 15 ml alcohol. This was left for 24 hrs and filtered yielding 0.70 g (29%) of a bright yellow-brown solid. This was triturated with ether several times, and the extracted product was recrystallised twice from alcohol, yielding a very bright yellow powdery solid whose crystalline form was difficult to determine. The melting point was 170^{o}. Analysis: C,70.45; H,5.38; N,4.25%. $C_{19}H_{17}NO_4$ requires

C,70.58; H,5.30; N,4.33%.

(F) Azobenzenes.

All the azobenzenes used were known compounds. Some were prepared as described in part I, some were available commercially and others were available in the department from previous studies. Only one was specially prepared.

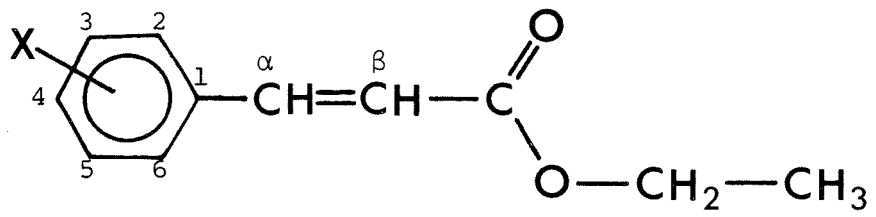
3-Fluoroazobenzene.

3-Fluoroaniline (0.50 g, 4.5 mmol) was dissolved in glacial acetic acid (25 ml) and steam-distilled nitrosobenzene (0.50 g 4.7 mmol) was added. The resulting solution was heated on a steam bath for 4 hours, cooled, and the solvent taken off under reduced pressure. The residue was taken up in benzene (35 ml), washed twice with dilute sodium carbonate solution, twice with water, and dried over anhydrous magnesium sulphate. After removing most of the solvent, the crude compound was columned on alumina (47 g), eluting with petroleum ether. The orange fraction gave an orange-red oil which solidified to thick needles or prisms, m.p. 41-42^{o} (lit. 44^{o}).[22] Its ^{13}C N.M.R. spectrum showed no impurities, so it was not purified further.

RESULTS

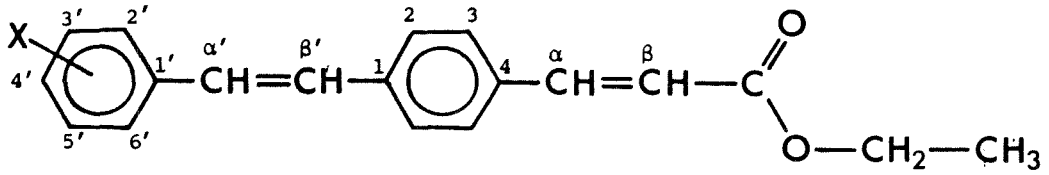
The ^{13}C N.M.R. chemical shifts of all the carbon atoms of the compounds studied are listed in the following pages. In all cases the chemical shift (δ) is quoted in p.p.m. downfield from tetramethylsilane. Figures followed by a question mark indicate uncertain assignments, while those given as only approximate were obtained visually rather than by computer print-out. Missing figures indicate that the peaks were not observed.

Ethyl Cinnamates



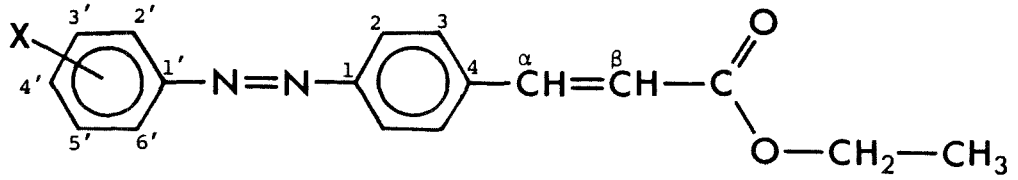
Substituent	Carbon C_1	C_2	C_3	C_4	C_5	C_6	C_α	C_β	>C=O	$-CH_2-$	$-CH_3$	-X
H	134.59	128.07	128.90	130.21	128.90	128.07	144.58	118.41	166.94	60.46	14.35	-
m-Me	134.53	128.77	138.52	131.05	128.77	125.26	144.76	118.14	167.04	60.42	14.34	21.29
p-Me	131.87	128.07	129.63	140.57	129.63	128.07	144.59	117.29	~166.3	60.37	14.35	21.44
m-F	{137.00 136.61	{114.88 113.76	?	{117.62 116.54	{130.66 130.23	{124.11 123.97	{143.26 143.10	119.79	166.59	60.67	14.30	-
p-F	{130.89 130.71	{130.11 129.71	{116.59 115.50	{~170.1 157.61	{116.59 115.50	{130.11 129.71	143.26	{118.20 118.06	166.83	60.54	14.35	-
m-Cl	136.39	127.81	134.98	130.09?	130.12?	126.20	142.92	119.87	166.51	60.65	14.29	-
p-Cl	133.04	129.19	129.10	136.17	129.10	129.19	143.10	118.98	~166.8	60.62	14.35	-
m-Br	136.64	130.75	123.06	132.97	130.36	126.62	142.80	119.87	166.46	60.65	14.29	-
p-Br	?	129.42	132.15	?	132.15	129.42	143.17	119.07	166.67	60.63	14.31	-
m-NO_2	136.32	122.42	~148.8	124.46	129.96	133.55	141.65	121.59	166.09	60.92	14.28	-
p-NO_2	140.66	128.65	124.20	?	124.20	128.65	141.63	122.68	166.02	61.01	14.29	-
p-OMe	127.29	129.71	114.35	161.41	114.35	129.71	144.25	115.85	167.33	60.30	14.37	55.36
p-NMe_2	122.45	129.73	111.91	?	111.91	129.73	145.10	112.74	?	60.05	14.44	40.13
m-NO	136.10	120.13	?	121.67	129.96	134.17	142.45	121.10	166.28	60.84	14.31	-
p-NO	140.95	129.00	121.36	?	121.36	129.00	142.29	122.63	166.08	60.95	14.28	-

Ethyl 4-(2-arylethenyl)cinnamates



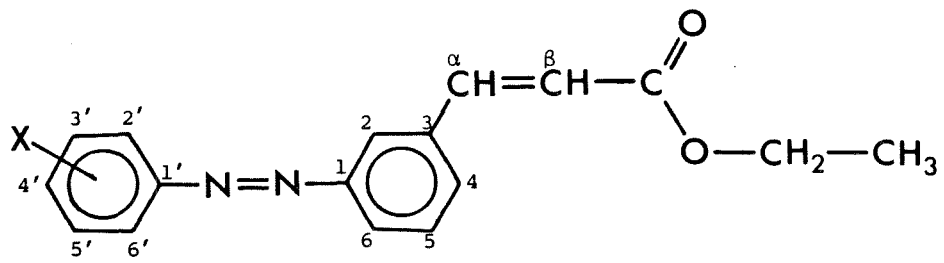
Substituent	Carbon $C_{1'}$	$C_{2'}$	$C_{3'}$	$C_{4'}$	$C_{5'}$	$C_{6'}$	$C_{\alpha'}$	$C_{\beta'}$	C_1	C_2	C_3	C_4	C_α	C_β	>C=O	$-CH_2-$	$-CH_3$	-X
H	136.99	126.69	128.74	128.01	128.74	126.69	130.09	127.80	139.33	126.93	128.50	133.69	144.03	117.86	167.01	60.46	14.34	-
m-Me	136.96	127.39	138.27	128.87	128.66	123.92	130.22	127.58	139.47	126.90	128.51	133.64	144.09	117.82	167.03	60.45	14.35	21.43
p-Me	134.21	126.64	129.48	137.98	129.48	126.64	130.07	126.79?	139.59	126.79	128.50	133.48	144.12	117.71	~167.4	60.44	14.35	21.28
m-F	?	{113.48 112.40	?	{115.31 114.25	{130.37 129.98	{122.71 122.57	{128.86 128.72	129.12	138.77	127.06	128.52	134.09	143.90	118.17	166.94	60.51	14.35	-
p-F	{133.29 133.11	{128.42 127.98	{116.26 115.18	{168.78 156.37	{116.26 115.18	{128.42 127.98	128.82	{127.63 127.54	139.16	126.85	128.51	133.73	143.99	117.92	166.99	60.45	14.35	-
m-Cl	138.91	126.46	134.76	127.87	129.92	124.90	128.51	129.19	138.77	127.07	128.51	134.07	143.89	118.16	166.94	60.50	14.35	-
p-Cl	135.49	127.82	128.94	133.63	128.94	127.82	128.66	128.41	138.95	126.94	128.51	133.93	143.89	118.06	166.93	60.49	14.35	-
m-Br	139.20	129.39	123.00	130.76	130.22	125.34	128.42	129.24	138.71	127.09	128.51	134.12	143.89	118.20	166.94	60.50	14.35	-
p-Br	135.92	128.12	131.87	~121.8	131.87	128.12	128.70	128.51	138.91	126.97	128.51	133.98	143.89	118.09	166.92	60.49	14.35	-
$m-NO_2$	138.81	121.00	148.76	122.32	129.62	132.32	127.29?	130.81	138.12	127.29	128.55	134.55	143.69	118.50	166.88	60.54	14.35	-
$p-NO_2$	143.40	127.03	124.16	?	124.16	127.03	127.46?	132.28	138.03	127.46	128.58	134.85	143.60	118.69	166.83	60.58	14.31	-
p-OMe	129.83	127.97	114.25	159.66	114.25	127.97	129.67	125.68	139.74	126.60	128.46	133.25	144.13	117.57	167.09	60.41	14.35	55.28
$p-NMe_2$	125.34	127.88	112.40	150.39	112.40	127.88	130.37	123.38	140.38	126.32	128.47	132.69	144.33	117.14	167.18	60.39	14.36	40.38

Ethyl 4-arylazocinnamates



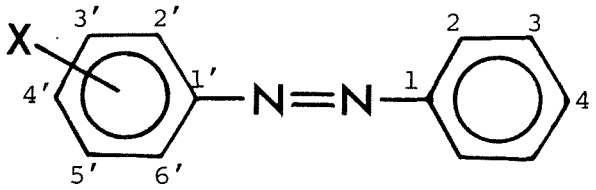
Substituent	Carbon $C_{1'}$	$C_{2'}$	$C_{3'}$	$C_{4'}$	$C_{5'}$	$C_{6'}$	C_1	C_2	C_3	C_4	C_α	C_β	>C=O	$-CH_2-$	$-CH_3$	-X
H	152.72	123.06	129.14	131.37	129.14	123.06	153.42	123.43	128.86	136.91	143.46	119.70	166.67	60.62	14.33	-
m-Me	152,77	123.17	139.00	132.16	128.94	120.65	153.46	123.35	128.84	136.78	143.50	119.57	166.69	60.60	14.32	21.34
p-Me	150.87	123.09	129.82	142.03	129.82	123.09	153.54	123.31	128.85	136.61	143.57	119.50	166.74	60.60	14.33	21.52
m-F	{154.29 153.94	{108.70 107.56	{169.52 157.12	{118.62 117.51	{130.51 130.09	{120.82 120.67	153.04	123.60	128.87	137.36	143.29	119.97	166.61	60.66	14.32	-
p-F	{149.30 149.15	{125.32 124.87	{116.71 115.56	{170.96 158.32	{116.71 115.56	{125.32 124.87	153.24	123.39	128.87	136.96	143.41	119.75	166.67	60.65	14.33	-
m-Cl	153.44	122.56	135.25	131.05	130.17	121.92	153.06	123.61	128.90	137.42	143.29	120.01	166.64	60.68	14.34	-
p-Cl	151.01	124.28	129.41	137.35	129.41	124.28	153.19	123.49	128.87	137.17	143.33	119.86	166.62	60.66	14.33	-
m-Br	153.50	124.76	123.09?	133.91	130.44	123.09	153.02	123.59	128.85	137.42	143.26	120.01	166.58	60.64	14.29	-
p-Br	151.33	124.49	132.39	125.84	132.39	124.49	153.16	123,51	128.86	137.21	143.31	119.87	166.60	60.65	14.33	-
m-NO_2	153.01	117.14	149.14	125.18	130.03	129.29	152.80	123.87	128.96	138.05	143.08	120.42	166.54	60.74	14.32	-
p-NO_2	155.66	123.58	124.76	~149.0	124.76	123.58	~153.2	124.01	128.98	138.32	143.01	120.60	166.51	60.75	14.26	-
p-OMe	147.12	125.04	114.32	162.46	114.32	125.04	153.61	123.13	128.85	136.26	143.62	119.29	166.77	60.58	14.34	55.57
p-NMe_2	143.85	125.34	111.54	152.75	111.54	125.34	154.26	122.75	128.86	135.22	143.96	118.58	166.94	60.51	14.35	40.28

Ethyl 3-arylazocinnamates



Substituent	Carbon $C_{1'}$	$C_{2'}$	$C_{3'}$	$C_{4'}$	$C_{5'}$	$C_{6'}$	C_1	C_2	C_3	C_4	C_5	C_6	C_α	C_β	>C=O	$-CH_2-$	$-CH_3$	-X
H	152.53	123.02	129.15	131.35	129.15	123.02	152.97	122.01	135.60	130.31	129.60	124.53	143.75	119.54	166.73	60.60	14.33	-
m-Me	152.65	123.16	139.06	132.15	128.97	120.66	153.05	122.00	135.58	130.23	129.60	124.49	143.81	119.50	166.75	60.60	14.35	21.35
p-Me	150.68	123.03	129.79	141.96	129.79	123.03	153.07	121.89	135.54	130.01	129.54	124.42	143.83	119.42	166.73	60.55	14.31	21.48
m-F	{154.13 153.79	{108.71 107.57	{169.53 157.12	{118.63 117.53	{130.55 130.12	{120.81 120.66	152.65	122.16	135.68	130.73	129.67	124.68	143.57	119.70	166.67	60.64	14.32	-
p-F	{149.15 148.99	{125.29 124.84	{116.71 115.56	{170.94 158.31	{116.71 115.56	{125.29 124.84	152.79	121.96	135.64	130.34	129.64	124.50	143.71	119.59	166.72	60.63	14.32	-
m-Cl	153.31	122.54	135.29	131.05	130.17	121.96	~152.66	122.16	135.74	130.76	129.67	124.69	143.59	119.71	166.69	60.64	14.34	-
p-Cl	150.81	124.25	129.40	137.30	129.40	124.25	152.73	122.02	135.59	130.54	129.65	124.58	143.63	119.59	166.71	60.64	14.30	-
m-Br	153.36	124.75	123.17	133.94	130.50	123.07	152.63	122.14	135.67	130.78	129.69	124.67	143.56	119.71	166.70	60.65	14.31	-
p-Br	151.21	124.46	132.41	125.81	132.41	124.46	152.76	122.03	135.65	130.59	129.67	124.59	143.61	119.64	166.69	60.64	14.31	-
m-NO_2	152.82	117.09	~149.0	125.22	130.07	129.34	152.44	122.31	135.79	131.34	129.82	124.89	143.35	119.91	166.59	60.69	14.30	-
p-NO_2	155.49	123.57	124.77	~149.0	124.77	123.57	152.69	122.42	135.89	131.54	129.85	124.95	143.25	120.03	166.56	60.71	14.32	-
p-OMe	146.89	124.95	114.29	162.39	114.29	124.95	153.09	121.71	135.50	129.71	129.53	124.32	143.91	119.33	166.76	60.57	14.33	55.57
p-NMe_2	143.57	125.19	111.48	152.64	111.48	125.19	153.60	121.41	135.33	128.75	129.41	124.05	144.26	118.98	166.87	60.49	14.32	40.21

Azobenzenes

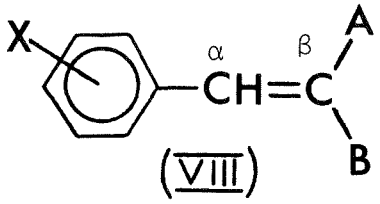


Substituent	Carbon $C_{1'}$	$C_{2'}$	$C_{3'}$	$C_{4'}$	$C_{5'}$	$C_{6'}$	C_1	C_2	C_3	C_4	-X
H	152.72	122.89	129.09	130.98	129.09	122.89	152.72	122.89	129.09	130.98	-
m-Me	152.79	122.99	138.95	131.78	128.89	120.50	152.79	122.84	129.05	130.85	21.33
p-Me	150.84	122.89	129.73	141.50	129.73	122.89	152.82	122.76	129.04	130.68	21.48
m-F	{154.38 154.04	{108.68 107.54	{169.51 ~157.1	{118.21 117.12	{130.41 130.02	{120.55 120.40	152.42	123.07	129.14	131.43	-
p-F	?	{125.09 124.64	{116.58 115.43	{170.69 158.09	{116.58 115.43	{125.09 124.64	?	122.84	129.09	131.00	-
m-Cl	153.51	122.35	?	130.70	130.12	121.87	152.44	123.08	129.14	131.49	-
p-Cl	151.01	124.12	129.34	?	129.34	124.12	152.53	122.96	129.14	131.25	-
m-Br	153.60	124.70	123.08?	133.58	130.41	122.91	152.37	123.08	129.14	131.50	-
p-Br	151.41	124.35	132.32	~125.3	132.32	124.35	152.53	122.98	129.14	131.29	-
m-NO_2	153.07	117.09	?	124.85	129.92	129.14	152.19	123.32	129.25	132.12	-
p-NO_2	155.71	123.43	124.71	?	124.71	123.43	~152.4	123.43	129.29	132.40	-
p-OMe	147.11	124.78	114.25	162.09	114.25	124.78	152.81	122.59	129.04	130.36	55.55
p-NMe_2	143.79	124.98	111.56	152.48	111.56	124.98	153.31	122.25	128.94	129.34	40.27

DISCUSSION

Interpretation of Data.

It has recently been established that the SCS of the β-carbon of styrene derivatives (VIII) is correlatable by means of



(VIII) (A,B constant)

the Hammett equation.[43,54,55,56] At the same time, it was demonstrated that some σ values show a substantial solvent dependence. Literature σ values are most often based on reactions and equilibria in aqueous or mixed aqueous organic solvents, and they do not necessarily apply in such solvents as deuterochloroform. In any particular series of styrene derivatives, all the C_β SCS's will be linearly related to the Hammett substituent constants applying in that solvent, but neither these σ values nor ρ values (which can also vary with solvent) are known. For the determination of transmission coefficients, which are based on relative ρ values, the constant factor in ρ cancels and true σ and ρ values are irrelevant, but for the discussion of the extent of resonance interaction between substituent and side-chain, σ values, while not essential, are useful in placing such interactions on a commonly used scale. For this reason, Hammett correlations in this study are based on the σ_m values derived by Happer and co-workers for carbon tetrachloride and deuterochloroform.[55] From correlations involving only meta-substituents, σ_p values were calculated assuming $\rho^{meta} = \rho^{para}$. Differences in σ_p between series

therefore reflect differences in resonance interaction between substituent and side-chain.

The Dual Substituent Parameter (DSP) equation of Ehrenson, Brownlee, and Taft[57] has also been widely used for the interpretation of SCS data for a wide range of carbon atoms in substituted benzene derivatives.[58]

$$SCS = \delta^X - \delta^H = \rho_I\sigma_I + \rho_R\sigma_R$$

Of the four σ_R scales (σ_R^-, σ_R^o, σ_R^{BA}, and σ_R^+), the one used is that which gives the best fit (as indicated by SD/RMS values) with meta- and para-substituents being treated separately. In this treatment, no $\rho^{meta} = \rho^{para}$ assumption is made, but two other difficulties arise. The first is that of solvent dependence of σ_I and σ_R. Any change in these is accommodated by a change in ρ_I or ρ_R respectively. The second difficulty arises from the assumption that one of the four σ_R scales can be applied to the system studied. This problem is discussed further on p.98.

In this work, DSP correlations were carried out where possible on the SCS's of all carbons except those in the ring carrying the variable substituent, and the C_β SCS's were also examined using the Hammett equation. The DSP correlations may be less reliable than normal because the substituents used are considerably fewer than the "minimum basis set" preferred by the authors of this approach.

Substituent Chemical Shifts of the β-Carbon.

In his work on the C_β SCS's of meta- and para-substituted β-nitrostyrenes, Happer[54] found that good Hammett correlations were obtained with Brown and Okamoto's σ^+ constants,[2] except

for those para-substituents capable of exerting -R effects. In further work on other β-substituted styrenes, Happer and co-workers[55] derived a set of σ_m values applying to each solvent used. They found that, in any particular solvent, although the meta-substituted members of each series could all be correlated by a single set of σ_m values, the magnitudes of the derived σ_p values varied according to the β-substituent(s) in the particular series. This means that there are variations in the amount of resonance interaction taking place, as indicated by the Yukawa-Tsuno r factor,[12] or by changes in $\lambda (= \rho_I/\rho_R)$ and/or the σ_R scale required in the case of the DSP equation. This is as expected, since more electron-withdrawing β-substituted ethenyl groups would place more demand for electrons on +R para-substituents. Later, Happer and Wright,[56] recognising the need for a "sliding σ_R scale" (rather than the discrete values σ_R^-, σ_R^o, σ_R^{BA}, and σ_R^+), derived a scale of electron demand, ε, which was based on the SCS's of many series of styrene derivatives, but was also applicable to reactivity data. They defined $\varepsilon_+ = 1.00$ (unit electron demand) for +R substituents in the styrene series. From this, it was found that in all series the σ_R of meta-substituents corresponded to $\varepsilon_+ = 0.15$, while for para-substituents, ε varied according to the β-substituent(s) present. For series such as β-nitrostyrenes[54] and β-acetylstyrenes[59] (and any reactivity data) which are correlated well by σ_p^+, it was found that $\varepsilon_+ = 1.8 - 2.0$. The β,β-dicyanostyrenes[55] have $\varepsilon_+ > 2$, and require σ_p values more exalted than σ^+. Series closely correlated by benzoic acid σ values (σ^{BA}), such as β,β-dimethylstyrenes

require ε_+ around 0.6 - 0.7 and σ^o was estimated to require $\varepsilon_+ \approx 0.4$. Series relevant to this study are the stilbenes (β-phenylstyrenes) for which $\varepsilon_+ = 1.12$ and the ethyl cinnamates (β-carboethoxystyrenes). Calculations based on the data in this work show that for the latter series $\varepsilon_+ = 1.4$, which means that ethyl cinnamates require σ_p values which are less exalted than σ^+ for +R substituents, but significantly more than σ^{BA}.

Transmission Coefficients

The C_β SCS's of the meta-substituted ethyl 4-arylethenyl-, 4-arylazo-, and 3-arylazocinnamates were correlated by least squares linear regression with the C_β SCS's of the corresponding meta-substituted ethyl cinnamates. The slopes obtained in these correlations represent the transmission coefficients for the three linkages, and are shown in Table VIII.

Table VIII

Transmission coefficients of the three linking groups studied.

Linking group	π'	SD/RMS
4-CH=CH-C_6H_4-	0.201	0.05
4-N=N-C_6H_4-	0.237	0.06
3-N=N-C_6H_4-	0.118	0.01

Bearing in mind that π' for the 4-azophenylene linkage varies according to the extent of interaction between the side-chain and the azo group (see Introduction), the value obtained in this work (0.24) lies in the expected range. It may be

compared with that obtained for electrophilic substitution (0.20) in Part I, and for diazonium coupling with R-acid (0.20),[10] where the extent of interaction would be rather low, as in the system studied here. The 4-ethenylphenylene linkage has a transmission coefficient (0.20) comparable to the azophenylene one. For the former linkage, the value of π' found for phenol ionization (0.15) is only about half of that obtained for the more strongly interacting 4-azophenylene linkage for the same reaction (0.28).[4d]

The value of π' for the 3-azophenylene linkage (0.12) is of particular interest because it is the first to be reported. It is surprisingly high, being almost exactly half of that for the corresponding 4-linkage. Jaffé has calculated a figure for the 3-phenylene linkage[60] of -0.013. One as high as 0.12 requires a fairly efficient mechanism for transmission of both inductive and resonance effects through the azo group to a side-chain meta-orientated to it.

Hammett Correlations of β-Carbon Data

The C_β SCS's of meta-substituted ethyl cinnamates, ethyl 4-arylethenylcinnamates, ethyl 4-arylazocinnamates and ethyl 3-arylazocinnamates were correlated against literature σ_m constants.[55] From these correlations, σ_p values were calculated assuming $\rho^{meta} = \rho^{para}$, and these are shown in Table IX.

Table IX

Calculated substituent constants and correlation parameters from Hammett correlations of C_β SCS's of Ar-Z-CH=CH-CO_2Et.

		-Z-			
Substituent	σ(ref.55)	-	4-CH=CH-C_6H_4-	4-N=N-C_6H_4-	3-N=N-C_6H_4-
H	0.00	0.00	-0.02	0.04	0.01
m-Me	-0.07	-0.07	-0.07	-0.10	-0.08
p-Me		-0.28	-0.21	-0.17	-0.25
m-F	0.35	0.35	0.37	0.33	0.35
p-F		-0.07	0.06	0.10	0.12
m-Cl	0.37	0.37	0.36	0.37	0.37
p-Cl		0.15	0.23	0.21	0.12
m-Br	0.38	0.37	0.41	0.37	0.37
p-Br		0.17	0.27	0.22	0.22
m-NO_2	0.80	0.80	0.78	0.81	0.80
p-NO_2		1.08	1.02	1.00	1.06
p-OMe		-0.65	-0.38	-0.39	-0.44
p-NMe_2		-1.43	-0.92	-1.15	-1.19
ρ		3.96	0.80	0.94	0.47
$\delta^H_{calc.}$		-0.01	0.02	-0.04	0.00
SD/RMS		0.01	0.05	0.06	0.01

As stated earlier, the ethyl cinnamate σ_p values are intermediate between σ^{BA} and σ^+ for +R substituents. Furthermore, the nitro group (-R) has a σ_p value intermediate between its accepted σ^o (0.81) and σ^-(1.25) values.[61] The σ_p values for the other three series are remarkably constant. In the 3-arylazo series, a change

in δ of 0.05 ppm results in a change in σ of 0.11 units. In spite of this, the p-chloro derivative of the ethyl 3-arylazocinnamates is the only compound where a clearly anomalous shift must be attributed to experimental error. The other major discrepancy is in the value obtained for the p-dimethylaminophenylethenylcinnamate, but this can be explained as arising from a weaker resonance interaction compared to that in both corresponding arylazo compounds.

As expected, the interposition of the linking group has decreased the degree of resonance in all three cases. A rough estimate of the transmission of resonance effects alone, $\pi'_{(R)}$, can be made by comparing the differences in chemical shifts between meta- and para-substituted members of a series with the same difference for the ethyl cinnamates, provided that $\rho^{meta} = \rho^{para}$ (a basic assumption of the Hammett treatment).

$$\pi'_{(R)} = (\delta^{p\text{-}X} - \delta^{m\text{-}X})_{series} \Big/ (\delta^{p\text{-}X} - \delta^{m\text{-}X})_{cinnamates}$$

A list of $\pi'_{(R)}$ values obtained in this way is given in Table X. It is not possible to determine inductive transmission coefficients, $\pi'_{(I)}$, in the same way, but the normal π' values should be a good approximation since these are based on meta-substituents and have only a small resonance component. Comparison of $\pi'_{(R)}$ with π' shows that all three linkages transmit +R effects less effectively than inductive effects. These conclusions are only tentative considering the approximations involved, together with the increased significance of experimental error in the chemical shift differences.

Table X

Calculated values of the resonance transmission coefficient, $\pi'_{(R)}$ for the three linking groups.

Substituent	4-CH=CH-C_6H_4-	4-N=N-C_6H_4-	3-N=N-C_6H_4-
Me	0.13	0.08	0.09
F	0.15	0.13	0.07
Cl	0.11	0.17	0.13
Br	0.14	0.18	0.09
NO_2	0.17	0.17	0.11
OMe[a]	0.13	0.15	0.08
NMe_2[a]	0.12	0.19	0.10
Mean[b]	0.13	0.15	0.09
π'	0.20	0.24	0.12

a. The δ^{meta} values for these are calculated ones based on data in other styrene series.

b. Mean $\pi'_{(R)}$ value for +R substituents, i.e. excluding NO_2.

The arylazo and arylethenyl groups belong to a relatively uncommon class of substituents which are -I and either +R or -R depending on circumstances. Substituent constants can be calculated for these groups from the substituent chemical shift relative to ethyl cinnamate, using the ethyl cinnamate Hammett correlation. These constants are shown in Table XI.

Table XI

Calculated substituent constants for the arylazo and arylethenyl substituents.

	Substituent		
X-	4-(X-C_6H_4-CH=CH-)	4-(X-C_6H_4-N=N-)	3-(X-C_6H_4-N=N-)
H	-0.14	0.33	0.29
m-Me	-0.15	0.29	0.28
p-Me	-0.18	0.28	0.26
m-F	-0.06	0.40	0.33
p-F	-0.12	0.34	0.30
m-Cl	-0.06	0.41	0.33
p-Cl	-0.09	0.37	0.30
m-Br	-0.05	0.41	0.33
p-Br	-0.08	0.37	0.31
m-NO_2	0.02	0.51	0.38
p-NO_2	0.07	0.55	0.41
p-OMe	-0.21	0.22	0.23
p-NMe_2	-0.32	0.04	0.15

In all cases except two, the 4-arylazo substituent has a greater σ value than the corresponding 3-arylazo substituent, which means that these substituents are acting as -I, -R groups. The same conclusion can be reached from the observed Hammett substituent constants for the phenylazo group based on benzoic acid ionisation (σ_m = +0.28, σ_p = +0.34),[4a] together with its σ_I of +0.25.[32a] In the case of the p-dimethylaminophenylazo substituent, $0<\sigma_p<\sigma_m$, which implies that this group is -I, +R. This leaves only the p-methoxy-

phenylazo substituent which has $\sigma_m = \sigma_p$ within experimental uncertainty. If it is assumed that $\rho_I^{meta} = \rho_I^{para}$, then (since $\sigma_I^{meta} = \sigma_I^{para}$) $\sigma_R^{meta} = \sigma_R^{para}$. This can only be true if both are equal to zero. The obvious interpretation is that there is no resonance interaction between the p-methoxyphenylazo group and the cinnamate ring, but a more likely situation is that π-interaction of both the +R and -R type exists simultaneously and they are equal in magnitude, so that there is no net transfer of charge. Since the overall resonance effect depends on the electronic character of both the substituent and the side-chain, it follows that any change in the latter will result in σ_R^{meta} and σ_R^{para} becoming non-zero. A stronger -R β-substituent will result in $\sigma_R^{para} < \sigma_R^{meta}$, while the opposite will be true for a weaker -R β-substituent.

The σ_p value of the phenylazo group, may be compared to that obtained from the C_β SCS of p-phenylazo-β-nitrostyrene, also in $CDCl_3$ solvent.[54] The σ_p value derived from this compound (0.23) is significantly lower than that derived from ethyl p-phenylazocinnamate (0.33), although it is still nowhere near a σ_p^+ value. This is in line with the anomalous σ_p values observed by Happer[54] for substituents capable of exerting both +R and -R effects, and attributed to both types of interaction occurring simultaneously but to different extents. The σ_m value of the phenylazo group obtained here, is in excellent agreement with literature values,[4a] in spite of the difference in solvents used.

The Hammett σ constants for the phenylethenyl group (σ_m = +0.03, σ_p = -0.07),[61] together with the estimated σ_I of +0.07,[61] show that normally it is a -I, +R group. This is also true in the ethyl cinnamate system (see Table XI) although the p-nitrophenylethenyl group appears to have a σ_R very close to zero.

From the ethyl cinnamate series, the substituent constants for the nitroso group were calculated as σ_m = +0.68 and σ_p = +1.07. They lie within the expected range. The σ_m value lies between those of the halogens and the nitro group. The removal of an oxygen atom from the nitro group would be expected to reduce its σ_I value (see Part I of this thesis and footnote 30 of reference 32b) and meta-effects are predominantly inductive in nature. Literature σ_I values for the nitro (+0.56) and nitroso (+0.34) substituents confirm this.[32a] On the other hand, σ_p is approximately equal to that for the nitro substituent, which suggests that an increased -R effect is compensating for a smaller -I effect. It is to be expected that σ_R for the nitroso group will be greater than that for the nitro group, since any -R interaction in the latter will result in an increase in negative charge on two oxygen atoms which are close together.[32b]

In addition to the cinnamate β-carbons discussed above, Hammett correlations were also carried out on the stilbenyl β-carbons in the stilbenes and the ethyl 4-arylethenylcinnamates. For this discussion, the latter series can be regarded as

4-carboethoxyethenylstilbenes. From the Hammett correlations, σ_p values were obtained, and these and other Hammett parameters are shown in Table XII together with those of the ethyl cinnamates (previously tabulated) for comparison.

Table XII

Calculated substituent constants and correlation parameters from C_β SCS correlations in ArCH=CH-Y

	-Y		
Substituent	$-CO_2Et$	$-C_6H_5$	$4-C_6H_4-CH=CH-CO_2Et$
H	0.00	-0.01	-0.01
m-Me	-0.07	-0.06	-0.06
p-Me	-0.28	-0.27	-0.28
m-F	0.35	0.35	0.35
p-F	-0.07	-0.05	-0.06
m-Cl	0.37	0.37	0.37
p-Cl	0.15	0.16	0.16
m-Br	0.37	0.38	0.38
p-Br	0.17	0.19	0.19
$m-NO_2$	0.80	0.80	0.80
$p-NO_2$	1.08	1.22	1.20
p-OMe	-0.65	-0.54	-0.57
$p-NMe_2$	-1.43	-1.13	-1.19
ρ	3.96	3.79	3.73
$\delta^H_{calc.}$	-0.01	0.05	0.02
SD/RMS	0.01	0.02	0.01

Comparing stilbene and ethyl cinnamate σ_p values shows that in the latter there is indeed a greater amount of resonance interaction between the side-chain and +R para-substituents, as expected. At the same time, the p-nitro group shows less -R interaction. In the 4-carboethoxyethenylstilbenes, slightly more resonance interaction is observed for strong +R para-substituents (p-OMe and p-NMe_2) than is the case in the stilbenes, but differences are small. In fact a rough comparison among different series of stilbenes variously substituted in the other ring (-H, 4-CH=CH-CO_2Et, 4-Cl, 4-NO_2, and 3-NO_2) shows that changes in ρ and σ_p (and consequently ε_+) are minimal. Stilbenes[44] (ρ = 3.8, ε_+ = 1.1) and 4-chlorostilbenes[44] (ρ = 3.8, ε_+ = 1.1) are practically identical, the 3-nitrostilbenes[44] have ρ = 4.4, ε_+ = 1.0, while the 4-carboethoxyethenylstilbenes (ρ = 3.7, ε_+ = 1.2) and 4-nitrostilbenes[44] (ρ = 3.8, ε_+ = 1.2), as expected, show slightly more interaction with +R para-substituents.

DSP Analysis of β-Carbon Data.

The greatest disadvantage of the DSP equation is the assumption that one σ_R scale applies to the system studied, for all substituents. The ±R nature of ethenyl side-chains results in resonance interaction occurring with both +R and -R para-substituents, which means that one σ_R scale will not suffice for DSP correlations of C_β SCS's when both types of para-substituents are involved. The simplest way to solve this problem is to carry out separate correlations

of +R and -R para-substituents. In this study, where only one -R substituent is involved, the simplest thing to do is to omit it altogether from the para-series. It was, however, included in meta-substituent correlations, since resonance contributions in this position are not great. The results of these correlations are shown in Table XIII, in which the same σ_R scale is used in all series in order to facilitate comparisons. The results support the conclusions drawn on the basis of the Hammett equation. This is not surprising considering that (a) $\lambda (= \rho_R/\rho_I)$ for meta-substituents is about the same as that normally found in other meta-series in which the Hammett equation is obeyed,[57] and (b) $\rho_I^{meta} \simeq \rho_I^{para}$, which is the major assumption of the Hammett equation.

Examination of the data for meta-substituted ethyl cinnamates, stilbenes, and 4-carboethoxyethenylstilbenes, shows nothing remarkable, with little variation in ρ_I^{meta} and λ^{meta}. The data for the para-substituted members of these series show greater variation in ρ_I^{para} and a larger λ^{para} for the ethyl cinnamates. In addition, the stilbenyl C_β SCS's are better correlated by σ_R^{BA} than by σ_R^+. This confirms the decreased amount of +R interaction occurring in the stilbenes compared to the ethyl cinnamates. Literature values for other styrene series[55] also show variations in λ^{para} and the σ_R scale required, according to the nature of the β-substituents in each series.

The DSP equation, when applied to the ethyl cinnamates, arylethenylcinnamates, and arylazocinnamates,

Table XIII

Results of DSP analysis of C_β resonances in all series. The p-nitro compound was omitted from para-substituent correlations.

Meta-substituents[a]

ArCH=CH-Y

-Y	ρ_I	ρ_R	λ	σ_R scale	SD/RMS
$-CO_2Et$	3.92	1.35	0.34	σ_R^-	0.02
$-C_6H_5$	3.86	1.22	0.32	σ_R^-	0.04
$4-C_6H_4-CH=CH-CO_2Et$	3.74	1.24	0.33	σ_R^-	0.03

Ar-Z-CH=CH-CO_2Et

-Z-	ρ_I	ρ_R	λ	σ_R scale	SD/RMS
$4-CH=CH-C_6H_4-$	0.82	0.23	0.28	σ_R^-	0.06
$4-N=N-C_6H_4-$	0.86	0.37	0.43	σ_R^-	0.08[b]
$3-N=N-C_6H_4-$	0.46	0.16	0.35	σ_R^-	0.02

Para-substituents

Ar-CH=CH-Y

-Y	ρ_I	ρ_R	λ	σ_R scale	SD/RMS
$-CO_2Et$	3.64	3.41	0.93	σ_R^+	0.05
$-C_6H_5$	3.13	2.60	0.83	σ_R^+	0.11[c]
$4-C_6H_4-CH=CH-CO_2Et$	3.10	2.72	0.88	σ_R^+	0.10[c]

Ar-Z-CH=CH-CO_2Et

-Z-	ρ_I	ρ_R	λ	σ_R scale	SD/RMS
$4-CH=CH-C_6H_4-$	0.73	0.45	0.61	σ_R^+	0.11[c]
$4-N=N-C_6H_4-$	0.86	0.66	0.77	σ_R^+	0.04
$3-N=N-C_6H_4-$	0.44	0.33	0.75	σ_R^+	0.08

a. While σ_R^- gave the best fit, σ_R^o or σ_R^{BA} did give acceptable ones.

b. σ_R^+ gave a better fit.

c. σ_R^{BA} gave slightly better fits.

can provide further insights into the transmission of inductive and resonance effects. The results of DSP treatment of these series are also shown in Table XIII. From these figures, $\pi'_{(I)}$ and $\pi'_{(R)}$ values were calculated for the three linkages. These are listed in Table XIV.

Table XIV

Inductive and resonance transmission coefficients for the three linking groups, based on DSP analyses of C_β SCS's.

Meta-substituents

Linking group	$\pi'_{(I)}$	$\pi'_{(R)}$	$\pi'_{(R)}/\pi'_{(I)}$
4-CH=CH-C_6H_4-	0.21	0.17	0.80
4-N=N-C_6H_4-	0.22	0.27	1.24
3-N=N-C_6H_4-	0.12	0.12	1.01

Para-substituents

Linking group	$\pi'_{(I)}$	$\pi'_{(R)}$	$\pi'_{(R)}/\pi'_{(I)}$
4-CH=CH-C_6H_4-	0.20	0.13	0.66
4-N=N-C_6H_4-	0.24	0.19	0.82
3-N=N-C_6H_4-	0.12	0.10	0.81

It is evident that $\pi'_{(I)}$ values for the three linkages are about the same as π' obtained from the Hammett equation. This is true for both meta- and para-substituents. The $\pi'_{(R)}$ values for the para-substituents also agree well with the approximate ones obtained from the Hammett equation except perhaps for the 4-azophenylene linkage. The abilities of the three linking groups to transmit resonance effects relative to inductive effects, $\pi'_{(R)}/\pi'_{(I)}$, are also given. The values

obtained for para-substituents in the three series show that the 4-ethenylphenylene linkage is possibly less effective than the azophenylene linkages at transmitting +R resonance effects. Of greater interest is the similarity of $\pi'_{(R)}/\pi'_{(I)}$ values obtained for the 3- and 4-azophenylene linkages, which means that both bridging groups transmit resonance effects with the same efficiency, relative to transmission of inductive effects. This is completely unexpected. One interpretation is that both inductive and resonance effects involve the π-orbitals, and that in extended conjugated π-systems such as these, any distinction between inductive and resonance effects becomes blurred into a general distortion of the π-system of the molecule. If this were the case, it makes the surprisingly high 3-azophenylene π' value easier to understand, since the extent of such distortion in a side-chain meta-orientated to the arylazo group could easily be about half of that in a para-orientated side-chain.

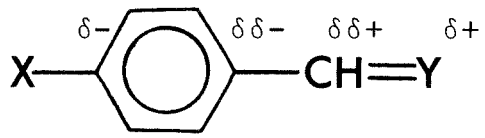
Discussion of α-Carbon Data

All studies of unsaturated side-chain α-carbons reported to date have shown that their SCS's are affected by ring substituents in the opposite way to that predicted on the basis of the substituents' electronic effects,[62] so that electron-withdrawing substituents, for example, result in upfield shifts of the C_α resonance. Such studies have also shown that the Hammett equation is not well suited to the correlation of C_α SCS's, but the DSP equation is more

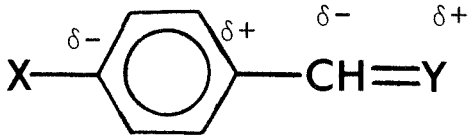
successful for this purpose. Brownlee and co-workers[62] have analysed data on a number of series of compounds, mostly with a carbonyl π-system, and concluded that the substituent inductive effect is predominant. They suggested that the reverse substituent effects are caused by localised polarisation (P_L) of the side-chain π-system, which is independent of polarisation of the extended π-system as a whole. Both types of polarisation are represented in Fig. III.

Fig. III

Extended polarisation, $P_{(E)}$, where X is a -I substituent:



Localised polarisation, $P_{(L)}$, where X is a -I substituent:



These workers attributed the P_L effect to a through-space electrostatic interaction between the C-X dipole and the π-system of the side-chain. To support this, they pointed out that ρ_I for meta-substituents is 20-30% greater than ρ_I for para-substituents, which are further away from the side-chain. On the basis of this interpretation, the C_α SCS's should constitute a useful probe for measuring direct field effects.

The SCS's of all α-carbons are presented in Table XV.

Table XV

Substituent chemical shifts for the α-carbon of Ar-Z-CH=CH-CO_2Et.

	-Z-			
Substituent	-	4-CH=CH-C_6H_4-	4-N=N-C_6H_4-	3-N=N-C_6H_4-
H	0.00	0.00	0.00	0.00
m-Me	0.18	0.06	0.04	0.06
p-Me	0.01	0.09	0.11	0.08
m-F	-1.40	-0.13	-0.17	-0.18
p-F	-1.32	-0.04	-0.05	-0.04
m-Cl	-1.66	-0.14	-0.17	-0.16
p-Cl	-1.48	-0.14	-0.13	-0.12
m-Br	-1.78	-0.14	-0.20	-0.19
p-Br	-1.41	-0.14	-0.15	-0.14
m-NO_2	-2.93	-0.34	-0.38	-0.40
p-NO_2	-2.95	-0.43	-0.45	-0.50
p-OMe	-0.33	0.10	0.16	0.16
p-NMe_2	0.52	0.30	0.50	0.51

They confirm that reverse substituent effects persist through extended systems, although they are smaller, as expected. Considering that in all three linking groups the distance between the C-X dipole and C_α is approximately the same, the magnitudes of the shifts should all be independent of the nature of the linking group. This is found to be true to within experimental error, for all except the p-dimethylaminophenylethenylcinnamate. However, if field effects alone were responsible for the shifts, each meta-substituted ethyl 4-arylazocinnamate should have the same shift as the corresponding para-substituted ethyl 3-arylazocinnamate.

That this is not so, indicates that other factors are also making a significant contribution.

The results of a DSP analysis of the C_α resonances are given in Table XVI.

Table XVI

Results of DSP analysis of C_α resonances in all series.

Meta-substituents

Ar-CH=CH-Y

-Y	ρ_I	ρ_R	λ	$\sigma_R$scale	SD/RMS
$-CO_2Et$	-4.20	-1.44	0.34	σ_R^o	0.10[a]
$-C_6H_5$	-3.71	-1.38	0.37	σ_R^o	0.12[a]
$4-C_6H_4-CH=CH-CO_2Et$	-3.98	-1.41	0.35	σ_R^o	0.11[a]

Ar-Z-CH=CH-CO_2Et

-Z-	ρ_I	ρ_R	λ	$\sigma_R$scale	SD/RMS
$4-CH=CH-C_6H_4-$	-0.46	-0.30	0.66	σ_R^o	0.03
$4-N=N-C_6H_4-$	-0.52	-0.26	0.49	σ_R^o	0.06
$3-N=N-C_6H_4-$	-0.54	-0.30	0.56	σ_R^o	0.06

Para-substituents

Ar-CH=CH-Y

-Y	ρ_I	ρ_R	λ	$\sigma_R$scale	SD/RMS
$-CO_2Et$	-3.91	-1.10	0.28	σ_R^{BA}	0.13[b]
$-C_6H_5$	-3.18	-0.61	0.19	σ_R^{BA}	0.14[c]
$4-C_6H_4-CH=CH-CO_2Et$	-3.57	-0.78	0.22	σ_R^{BA}	0.13[c]

Ar-Z-CH=CH-CO_2Et

-Z-	ρ_I	ρ_R	λ	$\sigma_R$scale	SD/RMS
$4-CH=CH-C_6H_4-$	-0.52	-0.42	0.80	σ_R^{BA}	0.11
$4-N=N-C_6H_4-$	-0.60	-0.59	1.00	σ_R^{BA}	0.11
$3-N=N-C_6H_4-$	-0.62	-0.62	1.00	σ_R^{BA}	0.10

a. σ_R^{BA} gave slightly better fits.
b. σ_R^o gave a slightly better fit.
c. σ_R^- gave slightly better fits.

In all cases, both ρ_I and ρ_R are negative. For the ethyl cinnamate and stilbenyl α-carbons, $|\rho_I^{para}| < |\rho_I^{meta}|$ but the difference is much smaller than the 20-30% observed by Brownlee for carbonyl carbons.[62] The λ^{meta} values for these α-carbons are smaller than those required with σ_R^o for a good Hammett fit; i.e. the chemical shifts show greater dependence on σ_I rather than σ_m. Values of λ^{para} are also small. In contrast, the α-carbons of the ethyl arylethenyl-cinnamates and arylazocinnamates, which are further away from the C-X bond, have roughly equal values of ρ_I^{meta} and ρ_I^{para}, and their λ^{meta} values are higher, bringing them into the region required for a good correlation with Hammett σ_m values. Values of λ^{para} are also much higher for these α-carbons.

Transmission coefficients for C_α inductive and resonance effects can be calculated in the same way as for C_β. These are given in Table XVII.

Table XVII

Inductive and resonance transmission coefficients for the three linking groups, based on DSP analyses of C_α SCS's.

Meta-substituents

Linking group	$\pi'(I)$	$\pi'(R)$	$\pi'(R)/\pi'(I)$
4-CH=CH-C_6H_4-	0.11	0.21	1.93
4-N=N-C_6H_4-	0.13	0.18	1.43
3-N=N-C_6H_4-	0.13	0.21	1.63

Para-substituents

Linking group	$\pi'(I)$	$\pi'(R)$	$\pi'(R)/\pi'(I)$
4-CH=CH-C_6H_4-	0.13	0.38	2.84
4-N=N-C_6H_4-	0.15	0.54	3.54
3-N=N-C_6H_4-	0.16	0.56	3.53

The value of $\pi'_{(I)}$ obtained for all three linkages is about 0.13. It is roughly equal to that of the 3-azophenylene linkage for normal (C_β) inductive effects, but substantially lower than that observed for the other two linkages. Since direct field effects should decrease in magnitude with distance according to an inverse square law, it should be possible to calculate an inductive transmission coefficient by constructing models and measuring distances between C-X bond and C_α. Such an exercise leads to a predicted transmission coefficient of 0.13, in excellent agreement with that obtained experimentally. The same calculation for C_β gives a $\pi'_{(I)}$ value of 0.20. This agrees moderately well with the measured transmission coefficient for normal (C_β) inductive effects for the 4-ethenylphenylene and 4-azophenylene, but not for the 3-azophenylene linkage, which suggests that the rate at which π-inductive effects fall off depends very much on the nature of the π-system.

Caution must be exercised in interpreting C_α resonance effects because it is difficult to tell whether ρ_R truly represents what it claims to, or whether it is a general "catch-all" term which includes other effects of unknown origin. Comparison of $\pi'_{(R)}/\pi'_{(I)}$ for para-substituents shows that the ethenylphenylene linkage transmits C_α resonance effects slightly less efficiently than the azophenylene linkages, as was observed for C_β. In contrast to C_β $\pi'_{(R)} > \pi'_{(I)}$ for C_α even for meta-substituents. This is a reflection of the faster rate of attenuation of direct field effects compared to resonance effects. Such behaviour

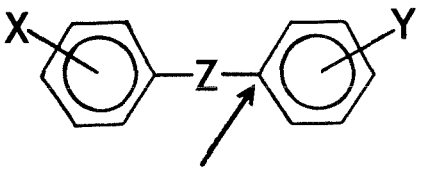
is also observed in the results of Brownlee and co-workers[62] where λ^{para} values for carbonyl carbons increase in going from benzoic to phenylacetic acids, or from acetophenones to methyl benzoates.

Discussion of Other Carbon Chemical Shifts

The chemical shifts of carbon atoms in the ring bearing the variable substituent were not examined in any detail. Previous studies have been carried out on both mono- and disubstituted benzenes,[58] and this study has nothing new to offer. It merely confirms the non-additivity of substituent effects already observed.

There is no evidence in the literature that the chemical shifts of any of the other carbons studied follow the Hammett equation. For this reason, only DSP correlations were carried out. The numbering system used is the same as in the Results Section.

(1) Correlations of 1-Carbon Resonances



Z=-CH=CH-, Y=-H, 4-CH=CH-CO_2Et.

Z=-N=N-, Y=-H, 3- or 4-CH=CH-CO_2Et.

DSP correlations of these carbons are summarised in Table XVIII. Like the α-carbon, C_1 also displays reverse substituent effects. The data fall into two groups depending on whether C_1 is bonded to an azo or an ethenyl group. The magnitude of ρ_I is about twice as great when an ethenyl group is attached. Values of λ^{meta} indicate that C_1's attached to an ethenyl group should give good Hammett correlations, but not those attached to an azo group.

Table XVIII

Results of DSP analysis of C_1 resonances in Ar-Z-C_6H_4-Y.

Meta-substituents

	ρ_I	ρ_R	λ	$\sigma_R$scale	SD/RMS
Z = -CH=CH-,					
Y = -H	-1.51	-0.57	0.38	σ_R^{BA}	0.03
Y = 4-CH=CH-CO_2Et.	-1.68	-0.69	0.41	σ_R^{BA}	0.05[a]
Z = -N=N-,					
Y = -H	-0.78	-0.20	0.26	σ_R^{BA}	0.09
Y = 4-CH=CH-CO_2Et.	-0.91	-0.16	0.18	σ_R^{BA}	0.05
Y = 3-CH=CH-CO_2Et.	-0.80	-0.16	0.20	σ_R^{BA}	0.07[b]

Para-substituents

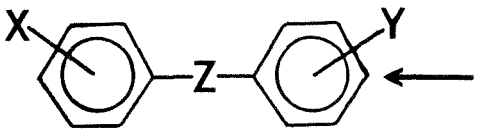
	ρ_I	ρ_R	λ	$\sigma_R$scale	SD/RMS
Z = -CH=CH-,					
Y = -H	-1.38	-1.18	0.85	σ_R^{BA}	0.03
	-1.30	-0.61	0.47	σ_R^{+}	0.20
Y = 4-CH=CH-CO_2Et.	-1.62	-1.41	0.87	σ_R^{BA}	0.05
	-1.51	-0.73	0.48	σ_R^{+}	0.20
Z = -N=N-,					
Y = -H	-0.71	-0.34	0.48	σ_R^{+}	0.15
Y = 4-CH=CH-CO_2Et.	-0.93	-0.49	0.53	σ_R^{+}	0.10
Y = 3-CH=CH-CO_2Et.	-0.60	-0.33	0.55	σ_R^{+}	0.32

a. σ_R^{o} gave a slightly better fit.

b. σ_R^{+} gave a slightly better fit.

Studies carried out previously on other phenyl ring carbons with various intervening linking groups, all confirm the reverse SCS's observed here, but no further comparisons can be drawn because of the dissimilarity in the nature of these linking groups to those studied here. Comparisons can be drawn, however, with the carbonyl carbons of the ethyl cinnamates and the cyano carbons of the trans-cinnamonitriles[63] (see p.115). In a similar way to the C_α's the shifts have been rationalised by Brownlee and co-workers[62] on the basis of localised polarisation of the phenylene π-system as a whole, although it is not clear why the linking group attached to C_1 should make such a large difference to its behaviour. A possible explanation is that the close proximity of the azo group results in strong resonance and inductive interactions which overshadow those of the much more distant variable substituent, resulting in a decreased dependence on substituent effects. Replacement of the azo bridge by the less strongly interacting ethenyl bridge increases ρ_I and ρ_R by different amounts.

(2) Correlations of 4-Carbon Resonances



Z=-CH=CH-, Y=-H, 4-CH=CH-CO_2Et.

Z=-N=N-, Y= -H, 3- or 4-CH=CH-CO_2Et.

These DSP correlations are shown in Table XIX. Normal substituents effects are observed. Differences in ρ_I between series are not great. Values of λ^{meta} suggest that good Hammett fits should be obtained, and values of λ^{para} suggest that resonance interactions are important in the C_4 chemical

shifts. No comparisons can be made with any literature data.

Table XIX

Results of DSP analysis of C_4 resonances in Ar-Z-C_6H_4-Y.

Meta-substituents

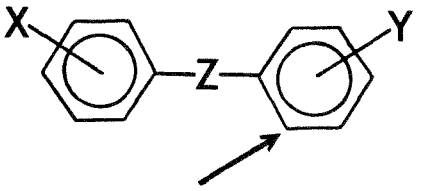
	ρ_I	ρ_R	λ	σ_R scale	SD/RMS
Z = -CH=CH-,					
Y = -H	1.16	0.38	0.32	σ_R^-	0.05
Y = 4-CH=CH-CO_2Et.	1.08	0.33	0.31	σ_R^-	0.06
Z = -N=N-,					
Y = -H	1.38	0.53	0.38	σ_R^-	0.02
Y = 4-CH=CH-CO_2Et.	1.38	0.53	0.39	σ_R^-	0.01
Y = 3-CH=CH-CO_2Et.	1.25	0.46	0.37	σ_R^-	0.03

Para-substituents

	ρ_I	ρ_R	λ	σ_R scale	SD/RMS
Z = -CH=CH-,					
Y = =H,	1.48	1.34	0.90	σ_R^{BA}	0.15[a]
Y = 4-CH=CH-CO_2Et.	1.34	1.35	1.01	σ_R^{BA}	0.09
Z = -N=N-					
Y = -H	1.72	1.99	1.16	σ_R^{BA}	0.10
Y = 4-CH=CH-CO_2Et.	1.73	2.03	1.17	σ_R^{BA}	0.11
Y = 3-CH=CH-CO_2Et.	1.54	1.85	1.21	σ_R^{BA}	0.11

a. σ_R^o gave a better fit.

(3) Correlations of 2-Carbon Resonances



Z=-CH=CH-, Y=-H, 4-CH=CH-CO_2Et.

Z=-N=N-, Y=-H, 3- or 4-CH=CH-CO_2Et.

Table XX

Results of DSP analysis of C_2 resonances in Ar-Z-C_6H_4-Y.

Meta-substituents

	ρ_I	ρ_R	λ	σ_R scale	SD/RMS
Z = -CH=CH-,					
Y = -H	0.40	0.13	0.34	σ_R^-	0.09
Y = 4-CH=CH-CO_2Et.	0.42	0.18	0.44	σ_R^-	0.05
Z = -N=N-,					
Y = -H	0.52	0.20	0.37	σ_R^-	0.03
Y = 4-CH=CH-CO_2Et.	0.51	0.23	0.45	σ_R^-	0.10[a]
Y = 3-CH=CH-CO_2Et, (C_2)	0.38	0.11	0.28	σ_R^-	0.08
(C_6)	0.43	0.17	0.39	σ_R^-	0.06

Para-substituents

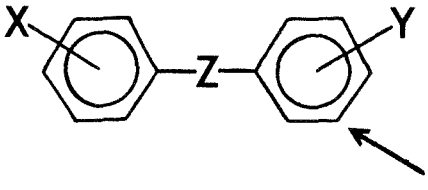
	ρ_I	ρ_R	λ	σ_R scale	SD/RMS
Z = -CH=CH-,					
Y = -H	0.53	0.68	1.28	σ_R^{BA}	0.20[a]
Y = 4-CH=CH-CO_2Et.	0.55	0.80	1.47	σ_R^{BA}	0.13[a]
Z = -N=N-,					
Y = -H	0.61	0.81	1.32	σ_R^{BA}	0.07
Y = 4-CH=CH-CO_2Et.	0.65	0.85	1.31	σ_R^{BA}	0.10
Y = 3-CH=CH-CO_2Et, (C_2)	0.46	0.73	1.60	σ_R^{BA}	0.12
(C_6)	0.47	0.61	1.28	σ_R^{BA}	0.11

a. σ_R^o gave better fits.

These DSP correlations are shown in Table XX. Normal substituent effects are observed. Again, λ^{meta} values indicate that the chemical shifts follow the Hammett equation closely.

It is interesting to compare the various ρ values obtained here with those applying to C_4. One might expect intuitively that resonance interactions at both these carbons would be roughly equal, and that inductive effects would be more strongly felt at the 2-position since it is closer to the substituent. This is not what is observed. The DSP analyses show that ρ_I and ρ_R for C_2 are smaller, but λ^{para} is greater. The explanation for this is based on Brownlee's interpretation that the phenylene group is polarised as a complete entity.[62] The carbons at each end of the polarised group, viz. C_1 and C_4 are the most influenced by P_L effects (see Fig. III, p.103) and have a higher ρ_I value. Because resonance effects are not influenced to the same extent by this consideration, λ^{para} for C_2 is greater than that for C_4 even though ρ_R is smaller.

(4) Chemical Shifts of the 3-Carbon

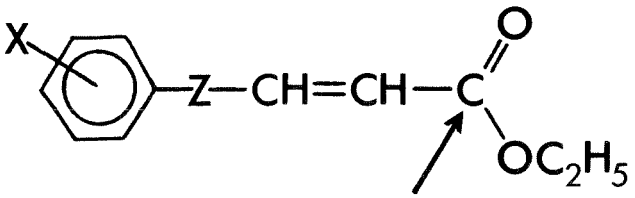


Z=-CH=CH-, Y=-H, 4-CH=CH-CO_2Et.
Z=-N=N-, Y=-H, 3- or 4-CH=CH-CO_2Et.

The SCS's for C_3 were so small (see Results) that no DSP correlations were attempted. However, by observing the shifts for the more "extreme" para-substituents, (nitro, methoxy, dimethylamino), it is possible to say with confidence that ρ

is positive. The low values can be explained by the same argument used for C_2 i.e. that they are in the middle of a group which is polarised as a complete entity. Hehre, Taft, and Topsom have also pointed out that π-inductive effects are smaller at the meta-position of monosubstituted benzenes.[64] In addition, no direct resonance interaction can occur between C_3 and the substituent. However, C_3 is conjugated with C_1 and in this respect it is noteworthy that ρ for C_3 is not negative. In the 3-arylazocinnamates, much higher ρ values are obtained for C_α and C_β in the side-chain than for C_3 and any through-bond substituent effects must necessarily pass through C_3. It could be that two much larger effects are operating at C_3 in opposition to each other, but it is impossible to tell from the present data because the effects of experimental uncertainty are too great.

(5) Correlations of Carbonyl Carbon Resonances.



Z = — (none),
4-CH=CH-C_6H_4-,
4-N=N-C_6H_4-,
3-N=N-C_6H_4-

Only the ethyl cinnamate carbonyl carbons have sufficiently large SCS's to enable them to be correlated. There is too much experimental uncertainty involved in attempting to correlate the other carbonyl groups, but even at these great distances, reverse substituent effects persist, i.e. ρ is negative. The results of DSP correlations for the ethyl cinnamates are as follows:

Meta-substituents:

ρ_I = -1.21, ρ_R = -0.51, λ = 0.43, SD/RMS = 0.06, σ_R^{BA} scale.

Para-substituents:

ρ_I = -1.16, ρ_R = -1.12, λ = 0.97, SD/RMS = 0.06, σ_R^{BA} scale.

-1.18, -0.74 0.63, 0.11, σ_R^+ scale.

First of all, it is evident from λ^{meta} that these carbonyl carbon shifts obey the Hammett equation. Secondly, the similarity of the DSP parameters to those of C_1 in the stilbenes and 4-arylethenylcinnamates is remarkable. This suggests that the nature of the bridging group (azo or ethenyl) is more important in determining SCS's than the π-system of the carbon itself. Further evidence for this comes from the cyano carbon shifts of trans-cinnamonitriles.[63] Comparison of the DSP parameters for all three types of carbons shows that they are remarkably similar.

Meta-substituents:

Stilbene C_1:

ρ_I = -1.5, ρ_R = -0.6, λ = 0.4, SD/RMS = 0.3, σ_R^{BA} scale.

Ethyl cinnamate >CO:

ρ_I = -1.2, ρ_R = -0.5, λ = 0.4, SD/RMS = 0.06, σ_R^{BA} scale.

Cinnamonitrile -CN:

ρ_I = -1.2, ρ_R = -0.4, λ = 0.3, SD/RMS = 0.18, σ_R^+ scale.

Para-substituents:

Stilbene C_1:

ρ_I = -1.4, ρ_R = -1.2, λ = 0.9, SD/RMS = -0.03, σ_R^{BA} scale.

Ethyl cinnamate >CO:

ρ_I = -1.2, ρ_R = -1.1, λ = 1.0, SD/RMS = 0.06, σ_R^{BA} scale.

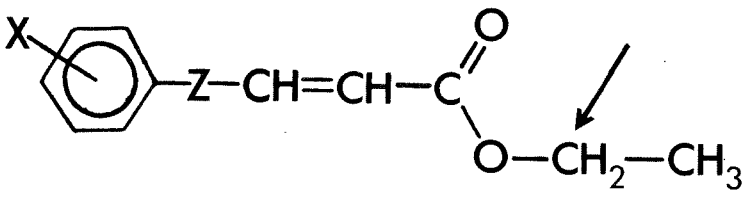
-1.2, -0.7, 0.6, 0.11, σ_R^+ scale.

Cinnamonitrile -CN:

ρ_I = -1.2, ρ_R = -1.1, λ = 0.9, SD/RMS = 0.08, σ_R^+ scale.

It is interesting to note that a stronger electron-withdrawing group attached to the carbon in question results in a greater λ^{para} value and a better fit with the σ_R^+ scale.

(6) Correlations of Methylene Carbon Resonances



Z = — (none),
4-CH=CH-C_6H_4-,
4-N=N-C_6H_4-,
3-N=N-C_6H_4-

The methylene group of the ethyl cinnamates exhibits sufficiently large SCS's to enable it to be correlated:

Meta-substituents:

ρ_I = 0.55, ρ_R = 0.20, λ = 0.36, SD/RMS = 0.07, σ_R^- scale.

Para-substituents:

ρ_I = 0.67, ρ_R = 0.56, λ = 0.84, SD/RMS = 0.07, σ_R^{BA} scale.

Again, λ^{meta} suggests that these shifts correlate well with Hammett σ_m values. Comparison of the DSP parameters with those obtained for C_2 in all other series, (Table XX, p.112) shows that they are practically identical. This is surprising, considering the dissimilarity in the nature of the two types of carbons. Not only is the methylene group saturated, but

it is also one atom further away than C_2 from the substituent, with an oxygen atom intervening. In spite of this, the only discernible difference between the two, is the slightly lower λ^{para} value pertaining to the methylene group. This is to be expected, because the saturated nature of the group would tend to suppress resonance effects. Nevertheless, resonance effects are still important in determining the chemical shift, as evidenced by the value of λ^{para} together with the σ_R scale used.

The methylene groups of the arylethenyl- and arylazocinnamates have SCS's which are too small to be meaningfully correlated, but their ρ values are positive.

(7) Chemical Shifts of the Methyl Carbon.

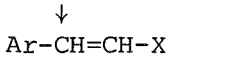
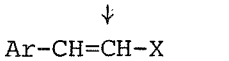
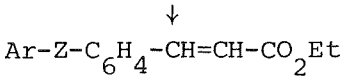
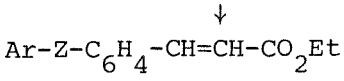
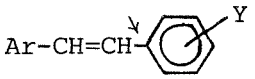
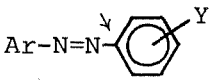
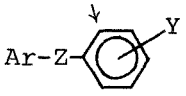
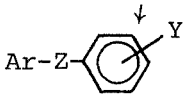
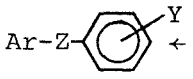
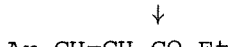
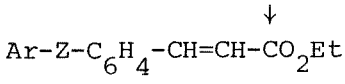
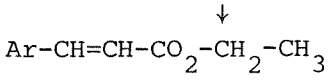
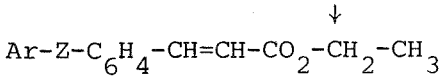
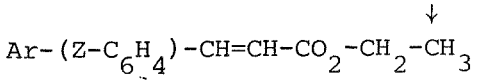
The methyl carbons of all series exhibit such small SCS's that the value of ρ is practically zero.

Summary

A summary of the behaviour of the chemical shifts of all carbon atoms discussed is given in Table XXI. In each case the quality of the Hammett fit (as indicated by SD/RMS) is shown, together with the sign of ρ and its approximate magnitude.

Table XXI

Summary of Hammett-like behaviour of chemical shifts of all carbon atoms discussed.

Carbon	Approximate ρ	Hammett fit (SD/RMS)	
	-3.5	Poor	(0.10)
	+3.8	Excellent	(0.01)
	-0.5	Good	(0.06)
	+0.8	Good	(0.05)
	-1.4	Good	(0.05)
	-0.7	Poor	(0.15)
	+0.4	Fair	(0.07)
	+ (small)	—	
	+ 1.3	Excellent	(0.03)
	- 1.1	Fair	(0.08)
	- (small)	—	
	+ 0.6	Good	(0.06)
	+ (small)	—	
	0	—	

X= $-CO_2Et$, $-C_6H_5$, $4\text{-}C_6H_4\text{-}CH{=}CH\text{-}CO_2Et$.

Y = -H, $-CH{=}CH\text{-}CO_2Et$.

Z = -CH=CH-, -N=N-.

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